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ABSTRACT

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The recently determined temperature dependence of the static oxygen polarizability anisotropy in tetragonal BaTiO_3 is incorporated in the Slater-Devonshire molecular theory of BaTiO_3 . The displaceable-Ti model is redefined in terms of relative ion shifts, and it is shown that this model reproduces the electrostatic properties of the actual case and is mathematically identical to the Slater model. The static polarizability anisotropy of the O_a -type oxygen in the tetragonal phase is expanded in a power series in the spontaneous polarization, and the molecular-model free energy function for the clamped crystal is derived and compared to the experimental function. An internal check on this model yields $(dB/dT) = 5.6 \times 10^{-15}$ (cgs), compared to the experimental value, 4.5×10^{-15} .

A zero-temperature calculation based on this model yielded a spontaneous polarization and Ti shift of 59,600 esu and $0.15\text{--}0.20 \text{ \AA}$, respectively, compared to the experimental data at room temperature, 77,000 esu and 0.16 \AA . Approximate zero-temperature calculations of the same nature are performed for PbTiO_3 , CdTiO_3 , SrTiO_3 , and CaTiO_3 using data extrapolated from the BaTiO_3 case. In this fashion the expected Curie points are ordered as follows with respect to decreasing temperature: PbTiO_3 , BaTiO_3 , CdTiO_3 , SrTiO_3 , and CaTiO_3 , which is the experimental order.

It is shown that a molecular model of BaTiO_3 consisting simply of Ti and O_a linear dipole chains at 0°K represents the best approximation to the actual crystal at room temperature. A calculation based on this model yields 72,000 esu and $0.15\text{--}0.20 \text{ \AA}$ for the spontaneous polarization and Ti shift, respectively, and the energy density plot for this model is practically identical to that for the complete molecular model.

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I. INTRODUCTION

The theoretical approaches to an understanding of the ferroelectric nature of BaTiO_3 have thus far been concerned with three distinct but complementary aspects of the phenomenon. The phenomenological theory of Devonshire ⁽¹⁾, ⁽²⁾, fashioned along the lines of similar theories of Rochelle salt by Mueller ⁽³⁾ and Cady ⁽⁴⁾, consists of expanding the free-energy function of the material in a power series of two sets of independent variables (e.g., polarizations and strains, polarizations and stresses), and assuming that this single function applies to all the various phases of the material. By examining the behavior of certain of the expansion coefficients the behavior of others can be inferred, and in this fashion Devonshire has been able to account for the dielectric, elastic, and piezoelectric properties of BaTiO_3 through three phase changes. These phenomenological free-energy expansions provide the touchstone for the discussion of the experimental data, and the data now available indicate that a single function is sufficient for the description of BaTiO_3 in the cubic, tetragonal, and orthorhombic phases.

The various molecular theories of BaTiO_3 have dealt, quantitatively and qualitatively, with the internal fields in this structure and the energy states of the Ti^{4+} ion or the TiO_6 octahedron; these theories are reviewed by Jona and Shirane ⁽⁵⁾. In particular, the molecular theory due to Slater ⁽⁶⁾ considers a displaceable Ti ion in a clamped (i.e., zero strain) BaTiO_3 unit cell and from the classical partition function an expression for the local field at the Ti site is obtained. This local field is then built into a Lorentz analysis of the polarizations which includes the electronic polarizabilities of the ions and the geometric Lorentz factors for

the perovskite structure. This analysis permits the external field to be written as a power series in the total polarization, and from this a free energy function is constructed for comparison with the phenomenological function. The salient features of Slater's treatment are the enhanced dipole-dipole coupling between the Ti and O_a ions along the polar axis (see Fig. 1) and the relatively negligible role of the Ba and O_b ions.

The recent approach taken by Cochran⁽⁷⁾ is to treat the onset of spontaneous polarization as a problem in lattice dynamics. Cochran considers the possible existence of a long-wavelength transverse-optical mode just above the Curie temperature. At the Curie point the frequency of this mode vanishes without any other modes in the crystal becoming unstable; it is shown that the " $4\pi/3$ catastrophe" is a consequence of this vanishing. Since this "catastrophe" condition is the mainspring of Slater's treatment, we see the interconnections of the various approaches. Capriciously enough, though, the transverse frequency of interest according to Cochran's calculations turns out to be about 10^{11} cps which is in the experimentally difficult millimeter wavelength range.

There are two aspects of the Slater-type molecular model which require further investigation, however, and it is the purpose of this paper to examine these items in detail. First, this model attributes the entire ionic polarization to the Ti ion, and second, no allowance is made for the temperature dependent anisotropy of the electronic polarizability of the ions.

It will be demonstrated using the neutron diffraction data on $BaTiO_3$ that a displaceable-Ti model may be defined which contains the essential dipolar features of the actual case and which is mathematically identical to the Slater model. Then, the recently determined anisotropy of the static oxygen polarizability in the tetragonal phase will be incorporated into the internal-field treatment along the lines of Slater, and the resulting free-

energy function will be compared to the experimental function to infer the potential energy constants of the Ti shift to 6th order. These potential energy data combined with the polarizability data will be used to compute the spontaneous polarization and Ti shift in BaTiO₃ based on the model according to a virtual work principle. This calculation will then be extended to other perovskite titanates (namely, PbTiO₃, SrTiO₃, CdTiO₃, and CaTiO₃) using data extrapolated from the BaTiO₃ data.

We shall have occasion in this study to employ experimental data on BaTiO₃, and the question of Curie temperatures arises. Accordingly we have adjusted the temperature scales on all data used such that the Curie temperature is 116°C to coincide with the polarizability data, reference (11).

All numerical calculations in this study were performed on the IBM 1410 at the R. P. I. Computing Laboratory, and Gaussian units are used throughout.

II. THE DISPLACEABLE-Ti MODEL

The displaceable-Ti model (alternately known as "rattling model") as first defined by Slater and later used by Kinase⁽⁸⁾ and others assumes that relative to the undisplaced lattice sites only the Ti ion is displaced, the other ions remaining at their lattice sites. This model attributes the entire ionic polarization to the Ti shift. The objections to this model stem from two sources: first, Devonshire⁽²⁾ has given arguments to show that the O_a ion is more easily displaced than Ti; and second, the neutron diffraction data of Frazer et al⁽⁹⁾ show that relative to the Ba ion positions the O_a shift is 1-1/2 times as large as the Ti shift in magnitude, and the O_b shift equals the Ti shift in magnitude.

These objections are really concerned with the problem of defining what is meant by ionic polarization, both on a microscopic and a macro-

scopic level. Considering the microscopic case, one is interested in calculating the local field at the actual site of the displaced ion and in relating this field expression to the undisplaced lattice sites so that the symmetry properties of the lattice translation vectors can be invoked. As an example, consider the field at an i^{th} ion site due to a j^{th} ion of charge q_j and zero electronic dipole moment when these two ions are shifted by $\underline{\delta_i}$ and $\underline{\delta_j}$ from their lattice sites, respectively. The straightforward multipole expansion of the Coulomb field at the i^{th} site yields

$$\underline{E_i} = -q_j \frac{\underline{R_{ij}}}{R_{ij}^3} + q_j \frac{3[(\underline{\delta_j} - \underline{\delta_i}) \cdot \underline{R_{ij}}] \underline{R_{ij}} - (\underline{\delta_j} - \underline{\delta_i}) R_{ij}^2}{R_{ij}^5} \quad (1)$$

where $\underline{R_{ij}}$ is the lattice translation vector between the i^{th} and j^{th} lattice positions. Eq (1) shows that microscopically the ionic polarization of a particular sublattice does not have a unique meaning but rather depends on what other sublattice is considered. Moreover, for $i = j$, Eq (1) shows that the bound charge density of the ionic polarization vanishes. These results are not new, having been first emphasized by Takagi (10), but the multipole expansion above is somewhat simpler. It is clear, then, that the microscopic local field definition involves relative rather than absolute shifts.

In view of this result we shall re-define the displaceable-Ti model as one which ignores the relative shifts between the Ba, O_a , and O_b sublattices and considers only the relative shift between the Ti and O_a sublattices. There is some experimental justification for such a model since the neutron diffraction data show the O_a and O_b sublattices shift approximately as a unit. These diffraction data indicate a relative shift between the Ba and O sublattices which our model ignores, but we are encouraged in this instance by Slater's calculations which show that the Ba role is small. We will now em-

pirically show that this model reproduces the local electric fields at the ion sites in BaTiO₃ quite satisfactorily by calculating those fields according to both this model and the actual case, using the neutron data. Before doing this, however, we can complete the above discussion of local fields at displaced sites by noting that to the usual order of approximation the electronic dipole interactions involve lattice sites rather than displaced sites as shown in a previous paper (11).

Turning to the local fields calculations, it will be convenient to employ a numerical designation for the ion types in the BaTiO₃ unit cell, and Fig.1 is a schematic drawing of the unit cell in the tetragonal phase with this arbitrary ion designation. Letting T_{ij} be the geometric Lorentz correction between i^{th} and j^{th} sublattices (e.g., $T_{12} = 30.080 + 4\pi/3$), the local field at the i^{th} ion site is given by (12)

$$E_i = \sum_j^5 T_{ij} \left[P_j + \frac{n_{je}}{\tau} (z_j - z_i) \right], \quad i = 1, 2, \dots, 5 \quad (2)$$

where P_j is the electronic polarization of the j^{th} sublattice, $(z_j - z_i)$ is the relative shift between the j^{th} and i^{th} sublattices, n_{je} is the effective ionic charge of a j^{th} type ion, and τ is the unit cell volume. The O_{b1} and O_{b2} ions are, of course, equivalent (#3 and #5) but the choice of 5 sublattices has the convenience of implying one ion type per unit cell. The procedure now is to invoke the electronic polarizability relations and to solve Eqs (2) for the P_j 's given the z_j 's from the neutron diffraction data. The details of the calculation are well known (12), and the T_{ij} are obtainable from Slater's paper (6). The static electronic polarizability data are taken from the author's previous paper (11) (we ignore here for comparison purposes the oxygen polarizability anisotropy to be treated in detail later)

$$\alpha_{Ti} = 0.186 \text{ \AA}^3; \alpha_o = 2.157 \text{ \AA}^3; \alpha_{Ba} = 2.33 \text{ \AA}^3$$

and the ion shifts relative to the Ba ion site are according to Frazer et al (9)

$$z_1 = 0.06 \text{ \AA}; z_2 = -0.09 \text{ \AA}; z_3 = z_5 = -0.06 \text{ \AA}$$

The n_j in Eqs (2) are assumed equal to the full ionic charges (Ba^{2+} , Ti^{4+} , O^{-2}), and the Eqs (2) solved for the P_j . The results of these calculations are shown in Table I under the heading "Actual Case". In this table the local fields, E_j , which are immediately obtainable by the polarizability relations from the P_j , are also given.

Similar calculations are now performed for the model we have defined above. According to that definition we have

$$Z = (z_1 - z_2) = (z_1 - z_3) = (z_1 - z_4) = (z_1 - z_5) = 0.15 \text{ \AA}$$

Substituting in Eq (2),

$$E_{i \neq 1} = \sum_j^5 T_{ij} P_j + \frac{n_i e}{\epsilon} Z T_{ii} \quad (3)$$

$$E_1 = \sum_j^5 T_{1j} P_j - \frac{e}{\epsilon} Z \sum_{j \neq 1}^5 n_j T_{1j}$$

However, Kinase (8) has shown that if one assumes that each ion carries the same fraction of its full ionic charge, then

$$\sum_{j \neq i}^5 n_j T_{ij} = -n_i T_{ii}$$

so that Eqs (3) can be written in the condensed form

$$E_i = \sum_j^5 T_{ij} P_j + \frac{e}{\epsilon} n_i Z T_{ii}, i = 1, 2, \dots, 5 \quad (4)$$

Now the Eqs (4) are identical to the field expressions developed by Slater and Kinase with the distinction that Z is identified here with the relative shifts between the Ti and O_a sublattices rather than an absolute shift from the cubic position. The solutions to the Eqs (4) are shown in Table I. The actual magnitudes in Table I are not of much real significance since we have assumed full ionic charges; but the relative magnitudes are significant for comparison purposes.

We see from Table I that the model reproduces the local field at the Ti and O_a sites to better than 1% accuracy, and it is just this fact which makes the model reasonable since the table also shows that this Ti- O_a interaction is the dominant interaction. And as anticipated, the Ba role is quite minor. We therefore conclude that as far as the microscopic field definitions are concerned, the model we have defined works very well because the O framework shifts more or less as a unit and because the highly polarizable Ba ions play a rather negligible electrostatic role.

Table I

Local Fields and Polarizations in $BaTiO_3$ (esu)

Ion	Actual Case		Model Case	
	$P_j \times 10^{-3}$	$E_j \times 10^{-6}$	$P_j \times 10^{-3}$	$E_j \times 10^{-6}$
Ti (#1)	7.45	2.59	7.53	2.61
O_a (#2)	70.0	2.08	70.0	2.09
O_b (#3, #5)	8.5	0.23	-0.47	-0.008
Ba (#4)	1.26	0.036	-4.37	-0.12

The above considerations apply to the microscopic definition of the local fields, and we now consider the macroscopic definitions. The electronic polarizations present no problem since the question of a proper reference frame is not involved; for the ionic polarization the proper macroscopic reference frame is the unpolarized crystal. Using the neutron diffraction data we find that the total ionic polarization is $66f (e/\zeta) \times 10^{-10}$ esu if either the Ba or O_b sublattice is taken as the macroscopic reference frame. The quantity f is the fraction of the full ionic charge carried by each ion and is assumed to be the same for all ion types. Based on our defined model we find $60f (e/\zeta) \times 10^{-10}$ esu. Since Triebwasser ⁽¹³⁾ has pointed out that the X-ray data of Kanzig ⁽¹⁴⁾ indicate that the Ba ions are not strongly affected by the ferroelectric transition, it is probably safe to take the Ba sublattice as the reference frame for the unpolarized crystal, and accordingly we see that our model satisfactorily reproduces the ionic polarization in the macroscopic sense.

In conclusion, then, we will take, as our displaceable-Ti model, that model which neglects the relative shifts between the Ba, O_a , and O_b sublattices and we shall assume that the total polarization (electronic plus ionic) associated with this model is the same as the measured polarization. The above empirical calculations demonstrate that this model contains the essential ingredients of the actual case and that the actual polarizations are reproduced to a quite good approximation. It is seen, however, that the effect of the model assumptions is to underestimate the total electronic and ionic polarizations. We should point out that the physical difference between the model here and Slater's model is the reference frame involved, and whereas the essential assumption to the latter model is that the other ions do not shift, the essential assumption in our model is that the total ionic polarization relative to the 0 framework is the same

as that relative to the unpolarized crystal.

III. OXYGEN POLARIZABILITY ANISOTROPY

Having examined the displaceable Ti model in some detail, we now turn to the problem of reliable electronic polarizability data which occupy such a central role in the Lorentz correction.

The static electronic polarizability data for the O_a and O_b oxygen ions in the $[001]$ - direction and the (001) -plane have been determined by the author⁽¹¹⁾ from the accurate refractive index data of Lawless and DeVries⁽¹⁵⁾ for tetragonal $BaTiO_3$. Arguments based on the optical absorption and X-ray emission data of $BaTiO_3$ were given to show that the large oxygen polarizability in materials containing TiO_6 octahedra is due to an exciton process involving excitations from the oxygen-2_p orbitals to the empty Ti-3d orbitals with degeneracy partially removed by the octahedral environment. Based on the known internuclear separations in $BaTiO_3$ at room temperature⁽⁹⁾ compared to the cubic phase, the anisotropic behavior of the oxygen polarizability as determined from the optical data was attributed to Ba- O_a overlap in the (001) - plane and Ti- O_a overlap in the $[001]$ -direction. The O_b polarizability in the cubic and tetragonal phases was considered the same (i.e., same temperature dependence) because the environment (overlap conditions) of this oxygen ion is not altered to the extent of the O_a environment across the ferroelectric transition.

These oxygen polarizability data for $BaTiO_3$ were extrapolated to zero frequency by comparison with the oxygen polarizability dispersion in $SrTiO_3$ and TiO_2 -rutile. The results of these studies are shown in Fig. 2, and it is seen that these overlap effects reduce the O_a polarizability in the $[001]$ - direction by about 15% from the extrapolated α_o value at room temperature. The data in

Fig. 2 were computed based on the assumption that the temperature dependence of the Ba and Ti polarizabilities are negligible.

We intend to incorporate the temperature dependence of α_{O_a} into the Lorentz correction of BaTiO_3 (the superscript [001] may now be deleted since we are discussing the tetragonal phase), and we note that this particular polarizability has a considerable effect on the calculated ferro-electric behavior judging from the large Ti-O_a dipole interaction shown in Table I. The explicit temperature dependence of this polarizability is probably small judging from the slight temperature dependence of α_0 and α_{O_b} in Fig. 2, and we shall therefore assume that this temperature dependence of α_{O_a} in the tetragonal phase arises entirely from the Ti-O_a overlap. Since this overlap is simply the relative shift between the Ti and O_a sublattices, it follows that the O_a polarizability can be expanded in a power series of the spontaneous polarization, P_s . Moreover, since the BaTiO_3 crystal structure is centrosymmetric, it is clear that this expansion will involve only even powers of P_s . Consequently, for reasons which will become clear later, we shall express $\alpha_{O_a} (= \alpha_2)$ as

$$\alpha_2(P_s) = \frac{\alpha_0}{1 + f(P_s)} \quad (5)$$

where

$$f(P_s) = K_1 P_s^2 + K_2 P_s^4 + K_3 P_s^6 \quad (6)$$

By α_o we shall mean the oxygen polarizability at 120 C at zero frequency, which from Fig. 2 is 2.157 \AA . The choice of expanding $f(P_s)$ to sixth order is to make this data correspond with the experimental data on BaTiO_3 (see below). The determination of the expansion coefficients in Eq (6) is a simple problem in least-squares curve fitting, since α_2 is given in Fig. 2 as a function of temperature and the spontaneous polarization is given as a function of temperature by Merz⁽¹⁶⁾. Combining these data we find

$$K_1 = 3.31 \times 10^{-11}, K_2 = -3.31 \times 10^{-22}, K_3 = -6.53 \times 10^{-32} \quad (7)$$

We now have sufficient data to approach the Lorentz correction problem which we take up in the next section, but before leaving this section we shall pursue these overlap-polarizability notions a bit further in relation to the optical properties. It has been demonstrated experimentally^{(17),(18)} that the birefringence in BaTiO_3 is approximately proportional to P_s^2 , and the usual theoretical reason given⁽¹⁹⁾ for this spontaneous Kerr effect is the quadratic electro-optic effect which relates changes in the index ellipsoid to the strains of the unit cell, and the strains are proportional to P_s^2 by electrostriction. This explanation implies that the unit-cell strains give rise to the birefringence. That this is not the whole story can be seen from the calculations by Kinase et al⁽²⁰⁾ of the birefringence: these authors include the strains in the Lorentz correction factors but assume isotropic polarizabilities, and they find that BaTiO_3 should be uniaxial positive with a birefringence of about 0.02, whereas, in fact, BaTiO_3 is uniaxial negative with a birefringence of about 0.06. Therefore, birefringence arising from the temperature-dependent overlap conditions between Ti and O_a is strong

enough to overcompensate the strain birefringence by a considerable amount. As mentioned above, the calculations leading to Fig. 2 included these strains. The arguments leading to the expansion Eq (6) imply that the overlap-polarizability birefringence can be expressed as a series in even powers of P_S , and so we may conclude that the total birefringence can be similarly expressed. But this does not necessarily mean that the birefringence in these type ferroelectrics will be proportional to P_S^2 , as other terms in the expansion may be required. In particular, in PbTiO_3 the birefringence first increases then decreases with decreasing temperature in the polar phase, in marked contrast to the BaTiO_3 case, although the c/a -ratio temperature dependence is very similar in the two materials ⁽²¹⁾. Kanzig has suggested that this behavior in PbTiO_3 is due to the increasing overlap of the ions with decreasing temperature ⁽²²⁾, but the above discussion indicates that this same mechanism is the dominant source of birefringence in BaTiO_3 , also.

IV. THE LORENTZ CORRECTION IN BaTiO_3

In this section we will construct a Gibbs free energy function based on the molecular model defined in Section II and incorporating the $\alpha_2(P_S)$ function, Eq. (5); and in the following section this model free energy will be compared with the corresponding experimental free energy.

The theoretical free energy of interest, A_p , refers to the clamped (zero-strain) crystal, and the independent variables are temperature and the spontaneous polarization, P_S . This function has the property ⁽⁶⁾

$$E_o = \left(\partial A_p / \partial P_S \right)_T \quad (8)$$

where E_0 is the external field. Consequently, we seek the relation $E_0(P_S)$ from the molecular model and in this way integrate Eq (8) to determine A_p relative to the unpolarized crystal. The groundwork for this discussion has been given by Slater⁽⁶⁾ and extended by Triebwasser⁽¹³⁾, and since we shall have occasion to refer to these papers we shall let Eq(S20) refer to Eq (20) in Slater's paper, etc.

The starting point for this discussion is the potential energy expansion describing the Ti ion shift(x,y,z) from the center of the oxygen octahedron (cubic symmetry), Eq (T16),

$$\begin{aligned} \Phi = & a(x^2+y^2+z^2)^2 + b_1(x^4+y^4+z^4) + c(x^6+y^6+z^6) + \\ & 2b_2(y^2z^2+x^2z^2+x^2y^2) + d_2x^2y^2z^2 + \\ & d_1[x^2(y^4+z^4) + y^2(z^4+x^4) + z^2(x^4+y^4)] \end{aligned} \quad (9)$$

This Ti shift is of course measured relative to the oxygen framework. Assuming that the Ti ions are independent, the partition function for the Ti displacements is found, and from this function the local field at the Ti site is derived in terms of the Ti ionic polarization, P_1' , relative to O_a . To fifth order Triebwasser gives, Eq (T17)

$$\begin{aligned} E_i = & (2a\tau/q^2) [1 + kT(3b_1 + 2b_2)/a^2] P_1' + \\ & (4\tau^3/q^4) [b_1 + (15/2)kTc/a] (P_1')^3 + \\ & (6\tau^5c/q^6) (P_1')^5 \end{aligned} \quad (10)$$

where we are interested in just one component of P'_1 , and where q is the charge on the Ti ion and τ is the unit cell volume (equal to $1/N$ in Triebwasser's notation where N is the number of ions per unit volume). In arriving at Eq(10) from Eq(9) the quantities d_1 and d_2 have been assumed approximately equal to c , an assumption which is justified below. This discussion so far neglects the effects of the other ions; that is, the Lorentz correction. To include the other ions we write for the local field at the i^{th} ion site

$$E_i = E_0 + \sum_j^5 T_{ij} P_j + T_{ii} P'_i, i = 1, 2, \dots, 5 \quad (11)$$

which is the same as Eq (4) except for the inclusion of the external field, E_0 . The Eqs (11) represent a set of simultaneous linear equation in the P_j 's after the polarizability relations are invoked, $P_j = (1/4\pi) X_j E_j$, in Slater's notation. These equations are solvable by determinants and one obtains E_0 in terms of E_1 and P'_1 , Eq (S33)

$$E_0 = (C_3/C_5) E_1 + 4\pi (C_4/C_5) P'_1 \quad (12)$$

However, Slater also shows that, Eq (S34)

$$P'_1 = (C_3/C_5) P_5 \quad (13)$$

where C_3 , C_4 , and C_5 are constants defined in terms of the polarizabilities and geometric Lorentz factors, Eqs(S20), (S24), and S (33). Consequently, substituting Eq(10) in Eq (12) and using Eq(13), we obtain $E_0(P_5)$ as required.

Now it is clear that the $\alpha_2(P_s)$ relation is involved in the solutions of Eqs (11), and it is found that the reciprocals of the X_j 's are involved. In particular,

$$(\overline{X}_2)^{-1} = (\overline{X}_0)^{-1} [1 + f(P_s)]$$

which is the reason we adopted the form Eq(5). Adopting Slater's notation for the T_{ij} 's in Eqs (11) we find that the effect of the changing O_a polarizability with P_s is to alter the quantities C_3 , C_4 , and C_5 in Eqs (12) and (13) as follows

$$\begin{aligned} C_3 &\longrightarrow C_3 - (C_6 + \overline{X}_{Ba} C_7) f(P_s) \\ C_4 &\longrightarrow C_4 - C_7 f(P_s) \\ C_5 &\longrightarrow C_5 - C_8 f(P_s) \end{aligned} \tag{14}$$

where we have defined

$$\begin{aligned} C_6 &= p \overline{X}_0 (\overline{X}_{Ba} + \frac{1}{2} p \overline{X}_{Ba} - 1) + \frac{1}{3} \overline{X}_{Ba} + \frac{2}{3} \overline{X}_0 - 1 \\ C_7 &= \frac{1}{3} + \overline{X}_0 \left[\frac{1}{2} q^2 (1 - \frac{1}{3} \overline{X}_{Ba}) - \frac{1}{3} (2q - p) - \frac{1}{6} p \overline{X}_{Ba} (2q + p) \right] \\ C_8 &= \overline{X}_0 (q + p) (1 + \frac{1}{2} p \overline{X}_{Ba}) - (1 + 2p \overline{X}_0) \end{aligned} \tag{15}$$

Eqs (15) are given in Slater's notation ($X_0 = X_3, X_{Ba} = X_4$, etc) and q and p are given in Eq (S12).

When the modified coefficients, Eq (14), are used in Eqs (12) and (13) we obtain the $E_0(P_s)$ relation with the effect of the changing O_a polarizability included. This function is then integrated according to Eq (8), and we find for the free energy relative to the unpolarized crystal,

$$A_p(P_s, T, x=0) = A(T) P_s^2 + B(T) P_s^4 + C(T) P_s^6 \tag{16}$$

where

$$A(T) = \frac{2\pi C_3 C_4}{C_5^2} + \left(\frac{C_3}{C_5}\right)^2 \frac{\alpha \tau}{e^2} + \left[\frac{C_3^2 \tau (3\beta_1 + 2\beta_2)}{C_5^2 e^2 \alpha} \right] kT \quad (17)$$

$$B(T) = \left(\frac{C_3}{C_5}\right)^4 \frac{\tau^3 \beta_1}{e^4} + \tau_1 \left[\left(\frac{C_3}{C_5}\right)^2 \frac{\alpha \tau}{e^2} + \pi \left(\frac{C_3 C_4}{C_5^2}\right) (C_9 + 1) \right] + \left[\left(\frac{C_3}{C_5}\right)^4 \frac{15 \tau^3}{2 e^4 \alpha} \gamma + \left(\frac{C_3}{C_5}\right)^2 \frac{\tau_1 \tau (3\beta_1 + 2\beta_2)}{e^2 \alpha} \right] kT \quad (18)$$

and

$$C(T) = \left(\frac{C_3}{C_5}\right)^6 \frac{\tau^5}{e^6} \gamma + \frac{1}{3} (2\tau_2 + \tau_1^2) \left(\frac{C_3}{C_5}\right)^2 \frac{\tau \alpha}{e^2} + \frac{8}{3} \tau_1 \left(\frac{C_3}{C_5}\right)^4 \frac{\tau^3}{e^4} \beta_1 + \frac{2\pi}{3} \left(\frac{C_3 C_4}{C_5^2}\right) (\tau_2 C_9 + \tau_2 + C_9 \tau_1^2) + \left[\left(\frac{C_3}{C_5}\right)^2 \left(\frac{2\tau_2 + \tau_1^2}{3}\right) \left(\frac{3\beta_1 + 2\beta_2}{e^2 \alpha}\right) + \left(\frac{C_3}{C_5}\right)^4 \frac{20 \tau^3 \tau_1}{e^4 \alpha} \gamma \right] kT \quad (19)$$

In arriving at Eqs (17) - (19) we have set q of Eq (10) equal to ne and employed the following definitions:

$$\alpha = a/n^2, \beta_1 = b_1/n^4, \beta_2 = b_2/n^4, \gamma = c/n^6$$

$$\tau_1 = K_1 [C_3 C_8 - C_5 (C_6 + X_{Ti} C_7)] / (C_3 C_5)$$

$$\tau_2 = (\tau_1 / K_1) [K_2 + (C_8 / C_5) K_1^2]$$

$$C_9 = K_1 (C_4 C_8 - C_5 C_7) / (\tau_1 C_4 C_5) \quad (20)$$

In Eqs (17) through (20) we of course mean by C_3 , C_4 , and C_5 the quantities defined by Slater. Eq (16) represents the model free-energy function with the changing O_a polarizability included through the \overline{V}_1 , and \overline{V}_2 terms. If $\overline{V}_1 = \overline{V}_2 = 0$, the $A(T)$, $B(T)$, and $C(T)$ coefficients reduce to the same as those given by Triebwasser, Eq (T18), allowing for the slight notational differences. It is interesting to note that the P_g -dependence of α_2 gives rise to a temperature dependence of $C(T)$ which is otherwise temperature independent in this approximation.

V. COMPARISON WITH THE EXPERIMENTAL FREE ENERGY FUNCTION

We now wish to compare our model free energy expression, Eq(16), with the experimentally determined function. However, the experimental and theoretical constraints are different and this must be taken into account. That is, the experimental situation is that of a "free" crystal (zero stress, X), whereas our theoretical expression is for a "clamped" crystal (zero strain, x). The prescription for this comparison has been given by Devonshire (1), (2) and used by Triebwasser (13), so that the development here does not vary in detail from Triebwasser's except for the numerical values.

The general starting point for this comparison is the free energy in the tetragonal phase in terms of the spontaneous polarization, P_s , and longitudinal strains, x_x, y_y , and z_z , relative to the unpolarized, unstrained crystal,

$$F(P_s, T, x) = \frac{1}{2} X^x P_s^2 + \frac{1}{4} \xi^x P_s^4 + \frac{1}{6} \zeta^x P_s^6 +$$

$$\frac{1}{2} C_{11}^P (x_x^2 + y_y^2 + z_z^2) + C_{12}^P (y_y z_z + x_x z_z + x_x y_y) +$$

$$g_{11} x_x P_s^2 + g_{12} (z_z + y_y) P_s^2 \quad (21)$$

where C_{11}^P and C_{12}^P are elements of the elastic constant tensor and where we are interested in only one component of P_s . The temperature dependence in Eq (21) is contained in the coefficients of P_s .

The corresponding experimental function is given by

$$F(P, T, X=0) = \frac{1}{2} \chi^X P^2 + \frac{1}{4} \xi^X P^4 + \frac{1}{6} \zeta^X P^6 \quad (22)$$

where χ^X , ξ^X , and ζ^X are measured as functions of temperature (see below). Comparison with Eq (16) shows that

$$\begin{aligned} A(T) &= \frac{1}{2} \chi^X \\ B(T) &= \frac{1}{4} \xi^X \\ C(T) &= \frac{1}{6} \zeta^X \end{aligned} \quad (23)$$

so it is clear that we seek relations between the coefficients of the stress-free energy, Eq (22), and the coefficients of the $F(P, T, x)$, Eq (21).

Since BaTiO₃ is not piezoelectric in the cubic phase and since our free energy functions are assumed to apply in all the phases, it follows that $\chi^X = \chi^x$, however, this neglects the effect of ordinary thermal expansion. If χ is written in the form of the Curie-Weiss law, $\chi = \chi_0 (T - T_0)$,

then as Devonshire ⁽¹⁾ shows, Eq (10.22),

$$\chi_0^X = \chi_0^x + \alpha_L (g_{11} + 2g_{12}) \quad (24)$$

The corresponding expression in Triebwasser's paper (Eq (24)) is in error by a factor of 2 -- the first of Eqs (23) shows the probable origin of this factor. For the coefficient of linear expansion in Eq (24), α_L , we adopt the value from Joho's recent,

very accurate X-ray data on cubic BaTiO_3 ⁽²³⁾ from 120°C-200°C, 1.083×10^{-5} per degree. The quantities g_{11} and g_{12} may be found from the relations developed by Devonshire⁽²⁾, Eq (2.4),

$$\begin{aligned} g_{11} + 2g_{12} &= -(Q_{11} + 2Q_{12})(C_{11}^P + 2C_{12}^P) \\ g_{11} - g_{12} &= -(Q_{11} - Q_{12})(C_{11}^P - C_{12}^P) \end{aligned} \quad (25)$$

where the Q's are elements of the electrostrictive tensor. The necessary compliances have been measured by Bond et al⁽²⁴⁾

$$C_{11}^P = 2.07 \times 10^{12}, \quad C_{12}^P = 1.40 \times 10^{12}$$

and the electrostrictive elements can be calculated from the spontaneous polarization data of Merz⁽¹⁶⁾ and the spontaneous strain data of Joho⁽²³⁾. This was done for four temperatures around room temperature and the average values found were

$$Q_{11} = 1.17 \times 10^{-12}, \quad Q_{12} = -0.583 \times 10^{-12}$$

Solving Eqs (25) we have

$$g_{11} = -0.794, \quad g_{12} = 0.383$$

These data differ somewhat from Triebwasser's due to the older Q-data used. From Eq (24), then

$$X_o^X = X_o^{\bar{X}} + 3.04 \times 10^{-7} \quad (26)$$

For the fourth-order coefficients, Devonshire⁽²⁾ gives,

Eq (2.4),

$$\xi_{11}^x = \xi_{11}^{\overline{x}} - 2g_{11}Q_{11} - 4g_{12}Q_{12}$$

so that substituting the above data we have

$$\xi_{11}^x = \xi_{11}^{\overline{x}} + 2.75 \times 10^{-12} \quad (27)$$

The experimental data necessary for the comparison of the 6th order coefficients are not available, and for the time being we will assume that these coefficients are approximately the same.

The necessary experimental data for the function Eq (22) are given by Drougard et al ⁽²⁵⁾ as follows in c.g.s. (the only system of units employed in this paper)

$$\chi^{\overline{x}} = 7.40 \times 10^{-5} (T - 383^\circ K)$$

$$\xi_{11}^{\overline{x}} = 18.0 \times 10^{-15} (T - 448^\circ K)$$

$$g_{11}^{\overline{x}} = 54 \times 10^{-23}$$

(28)

The temperature dependence of $g_{11}^{\overline{x}}$ is not given, but there is some evidence that this coefficient is temperature dependent: Merz ⁽¹⁶⁾ gives 22.8×10^{-23} at 120° C for this coefficient, and Huibregtse et al ⁽²⁶⁾ give 72×10^{-23} at 8° C.

From Eqs (27) and (28) we find that at the Curie point

$$\epsilon_{\parallel}^{\text{X}} = -0.99 \times 10^{-12}, \quad \epsilon_{\parallel}^{\text{K}} = 1.76 \times 10^{-12}$$

and it can be shown⁽²⁷⁾ as a consequence of this that the clamped crystal undergoes a second-order transition while the free (actual) crystal undergoes a first-order transition, as observed.

Finally, combining Eqs (26), (27), and (28), we have

$$A(T) = 3.715 \times 10^{-5} T - 1.422 \times 10^{-2}$$

$$B(T) = 4.50 \times 10^{-15} T - 1.327 \times 10^{-12}$$

$$C(T) = 9 \times 10^{-23}$$

(29)

Eqs (29) are now combined with Eqs (16) through (19) using the auxiliary definitions and polarizability data Eq (7); the static electronic polarizabilities quoted in Section II are employed, and the unit cell volume is taken from Joho's data at 120° C, $64.45 \times 10^{-24} \text{ cm}^3$. This comparison allows us to solve for the modified force constants, α , β_1 , β_2 , and γ ; however, Eqs (29) represent five equations whereas we have four unknowns. Consequently, following Triebwasser, we shall use the dB/dT equation as a check on the calculations.

These calculations were performed for two cases: a so-called "Anisotropic Case" and an "Isotropic Case", where for the latter case $\overline{\nu}_1$ and $\overline{\nu}_2$ were set equal to zero in Eqs (17) through (19) and this of course amounts to letting the 0_a

polarizability be isotropic and equal to the O_b value. The results of these computations are shown in Table II.

Table II

Modified Force Constants for the Ti Shift
(c.g.s.)

	Anisotropic Case	Isotropic Case ^(a)
α	1.05×10^5	1.05×10^5
β_1	-8.63×10^{20}	-1.31×10^{19}
β_2	1.65×10^{21}	3.75×10^{20}
γ	3.71×10^{36}	4.59×10^{34}
(dB/dT) ^(b)	5.63×10^{-15}	0.046×10^{-15}

(a) Obtained by setting $\sigma_1 = \sigma_2 = 0$ in Eqs (17) through (19)

(b) Experimental value: 4.5×10^{-15}

The value for γ for the Anisotropic Case is fairly insensitive to which of the three $S_{///}^2$ values quoted above is employed; the value at 8° C was selected, 72×10^{-23} cgs, for calculating in Table II for both cases. To test the sensitivity of the Anisotropic-Case results to the expansion coefficients, Eq (7), a fourth-order fit to Eq (6) was performed and the resulting coefficients used in Eqs (17) through (19).

The results were the same as for the sixth-order fit to within a few percent ($\beta_1 = -9.02 \times 10^{20}$, $\beta_2 = 1.71 \times 10^{21}$, $\gamma = 4.46 \times 10^{36}$, $(dB/dT) = 6.47 \times 10^{15}$ for the fourth-order fit).

Comparing the results in Table II we first note the good agreement of (dB/dT) for the Anisotropic Case with the experimental value, whereas for the Isotropic Case there is a discrepancy of two orders of magnitude. This agreement provides a valuable internal check on the molecular model and on the assumptions used, and underscores the importance of including the polarizability anisotropy.

From Table II, the effect of the $\phi_2(P_s)$ function is to "soften" the potential energy curve, ϕ , for small displacements; i.e., β_1 , for the Anisotropic Case is smaller than the corresponding value for the Isotropic Case. In neither case, however, does ϕ have a minimum other than the origin. The reason for this alteration in ϕ is due to the decreased polarizability of O_a with the Ti shift. Consequently, for an equivalent Ti shift, the resulting polarization energy for the Anisotropic Case is larger (smaller negatively) than for the Isotropic Case, and correspondingly the value of which balances the negative polarization energy needn't be as large for the former case as for the latter.

Regarding the temperature dependence of $C(T)$ in Eq (19) we find on substituting the appropriate quantities, $dC/dT = 0.53 \times 10^{-24}$, whereas the experimental data quoted above indicate $dC/dT \sim -10^{-24}$. This discrepancy is sign probably originates from the fact that $\sum_{i=1}^X$ was not corrected to the zero-strain value due to insufficient data. Additional experimental data is needed to clarify this situation. Moreover, the procedure for treating the experimental data according to Eq(22)

has been to assume that this sixth-order coefficient is temperature-insensitive⁽²⁷⁾.

In this section we have compared the free energies from the model and from experiment and found that the model defined in Section II represents a good approximation when the changing polarizability of O_a is included in the Lorentz correction. In a certain sense, however, we have been dealing with numerology here, and in the next section we will consider a zero-temperature calculation of the spontaneous polarization and Ti shift. This calculation will be based on the molecular model we have defined and will minimize the potential energy of a $BaTiO_3$ unit cell using the data we have developed in this and preceding sections.

VI. A MINIMUM ENERGY CALCULATION

A test of the displaceable-Ti model and the associated numerical constants determined in the previous section is provided by a zero-temperature calculation wherein we minimize the potential energy per unit cell volume taking account of the detailed Lorentz corrections at all the ion sites.

Limiting ourselves to Ti shifts along the z-axis to correspond with the tetragonal phase, the potential energy per unit volume to be minimized is given by

$$u - u^0 = \frac{1}{2} (a z^2 + b z^4 + c z^6) - \frac{1}{2} P' E - \sum_j^5 \int P_j dE_j \quad (30)$$

The last term in Eq(30) represents the total electronic polarization energy per unit volume, since ⁽²⁸⁾ $dU = -pdE$, and u^0 is the unpolarized energy density. The factor 1/2 in the third term arises from the fact that in the absence of an external field we must count dipole interactions once, not twice. Invoking the polarizability relations, $P_j = (\alpha_j/\epsilon)E_j$, and writing $z = \epsilon P_1'/ne$, Eq(30) becomes,

$$u - u^0 = (\epsilon/e^2) \left[\alpha (P_1')^2 + \beta (\epsilon/e)^2 (P_1')^4 + \gamma (\epsilon/e)^4 (P_1')^6 \right] - (\epsilon/2\alpha_1) P_1 P_1' - \frac{1}{2} \sum_{j \neq 2}^5 \frac{\epsilon}{\alpha_j} P_j^2 - \frac{\alpha_3}{2\epsilon} \int_0^{P_2} \frac{d(E_2^2)}{1 + f(P_2)} \quad (31)$$

where α , β , and γ are the modified force constants discussed in the previous section, and we have used Eq(5) in the last term of Eq(31).

Consider the integral in Eq(31) representing the 0_a electronic polarization energy. It is clear from the discussion in Section IV that E_2 may be written in terms of P_s as

$$E_2 = a_1 P_s + a_2 P_s^3 + a_3 P_s^5 \quad (32)$$

If Eqs (6) and (32) are substituted in this integral and if the denominator of the integrand is expanded in powers of P_s , we find after integrating that the resulting terms can be arranged to a very good approximation as

$$- \left(\frac{\alpha_3 E_2^2}{2\epsilon} \right) \left(1 - \frac{1}{2} K_1 P_s^2 - \frac{1}{4} K_2' P_s^4 - \frac{1}{6} K_3' P_s^6 \right) \quad (33)$$

where K_1 is defined by Eq(6) and

$$K'_2 = \frac{4}{3}(K_2 - K_1^2)$$

$$K'_3 = \frac{3}{2}(K_1^3 + K_3 - 2K_1K_2) \quad (34)$$

The form Eq(33) has the advantage that a_1, a_2 , and a_3 of Eq (32) are not involved, and the approximation involves 6th order terms (i.e., to fourth order in P_s , Eq(33) is exact).

The energy per unit volume, $u-u^0$, is minimized as follows: for a given value of P'_1 , Eqs (4) are solved for the P_j and for E_2 using the polarizability relations, and from these solutions P_s is found. These quantities are substituted in Eq (31) using Eq (33) to determine $u-u^0$. A new value for $u-u^0$ is obtained by perturbing P'_1 , and in this fashion the minimum energy is found by a relaxation technique on a digital machine. In solving Eqs (4) the $\alpha_2(P_s)$ relation Eq (5) must be employed, and for convenience in the numerical calculations it is desirable to reformulate this relation as $\alpha_2(P'_1)$. The details of this reformulation will not be displayed since it is clear from Eqs (13) and (14) how this is to be done.

These calculations were programmed using the Isotropic-Case and Anisotropic-Case data in Table II. For the former case, the $f(P_s)$ function was of course set equal to zero. From the discussion in Section II, there is a third case of interest, also; namely, the case which neglects the B_a and O_b polarizations and considers only the linear dipole chains of Ti and O_a along the polar axis. For this case, the α_3 and α_4 polarizabilities were not set equal to zero in formulating $\alpha_2(P'_1)$ from $\alpha_2(P_s)$,

but rather the P_3 , P_4 , and P_5 polarizations in Eqs (4) were set equal to zero in the relaxation technique. This third case was also programmed using the Anisotropic-Case data, and the results of these calculations are shown in Table III.

Table III

Zero-Temperature Approximation of
Tetragon BaTiO_3

	Isotropic Case (Ba,Ti, O_a , O_b)	Anisotropic Cases (Ba,Ti, O_a , O_b) (Ti, O_a) ^(a)	
P_s (esu)	667,000	59,600	71,700
P_1/P_s	37.8%	53.2%	44.2%
P_2/P_s	59.6%	58.4%	50.2%
P_3/P_s	-.07%	-6.6%	0
P_4/P_s	-3.6%	-5.3%	0
$nZ, \text{\AA}$	3.39	0.422	0.425

(a) Obtained by setting $P_3 = P_4 = P_5 = 0$.

The experimental value of the spontaneous polarization in the tetragonal phase ranges from 55,000 to 78,000 esu, being about 77,000 esu at room temperature.⁽¹⁶⁾ Therefore, the Isotropic Case calculation in Table III as an order of magnitude too high, but the Anisotropic Case data agree quite well.

Moreover, the latter data represent a good approximation to the room-temperature behavior since the discussion in Section II shows that the model underestimates the total polarization by about 25%. If the $(\text{Ba}, \text{Ti}, \text{O}_a, \text{O}_b)$ P_s for the Anisotropic Case is corrected for this underestimation we find 79,000 esu.

The neutron diffraction data of Frazer et al⁽⁹⁾ mentioned in Section II show that experimentally Z is about 0.16 \AA at room temperature. To compare our calculated data with this value we require n , the number of electronic charges on the Ti ion. Kinase and Takahashi⁽²⁹⁾ have developed a quantitative molecular theory for the spontaneous deformation of BaTiO_3 according to the Slater displaceable-Ti model, and these authors find good agreement with the measured deformation properties of the tetragonal phase if n is taken as 2.12. Alternately, Eqs (4) can be solved for f (defined in Section II) by using the known polarizabilities, unit cell volume, ion shifts relative to Ba (or O_b), and the spontaneous polarization, all at room temperature. This calculation, which assumes f to be the same for all ion types, was carried out by an iteration procedure on a digital machine, and it was found that $n = 4f = 2.80$. It is not surprising that this value of n is somewhat larger since the calculation employs smaller oxygen polarizabilities (infinite wavelength) compared to the previous isotropic oxygen polarizability⁽⁶⁾. From Table III, then, we find $Z = 0.15 - 0.20 \text{ \AA}$ for the Anisotropic Case using the above n -values, whereas for the Isotropic Case, $\sim 1.5 \text{ \AA}$.

Therefore, there is excellent agreement between the results of these calculations for the Anisotropic Case and the experimental data. It is reasonable to ask why this clamped crystal approximation at 0°K represents the actual crystal at room temperature so well. There are two reasons for this in addition to the electrostatic arguments given in Section II. First, the strain of the unit cell introduces

additional ionic polarization (regardless of the reference frame) and at the same time decreases the Lorentz correction at the Ti and O_a sites⁽¹¹⁾, thus decreasing the electronic polarization. Consequently, there is some cancellation between these two effects. Secondly, the strain energy terms in Eq (21) (the last four terms) when evaluated using room temperature data are seen to contribute negatively to $F(P_s, T, x)$, and so there is some cancellation between these strain energy terms and the positive energy terms that depend linearly on temperature (e.g., $\chi_o^x T P_3^2$ etc). The physical reason for the decrease in the internal energy arising from the strain terms is due to the slight volume increase in going from the cubic to the tetragonal phase⁽²³⁾. Therefore, the electrostatic and energy differences between the clamped crystal at 0°K and the actual crystal at room temperature tend to cancel and the former case represents a good approximation to the latter case.

From Table III, it is seen that the (Ti, O_a) Anisotropic Case contains the essential ingredients of the phenomenon, and interestingly enough represents a better model than the (Ba, Ti, O_a, O_b) case because by neglecting the P_3 and P_4 polarizations the spontaneous polarization, P_s , is not underestimated as in the latter case.

On the basis of the results in Tables II and III we conclude that the incorporation of the temperature-dependent overlap effects on α_2 brings the calculated results into very good agreement with the experimental data on $BaTiO_3$. Our picture here of ferroelectricity in $BaTiO_3$ is one explainable in terms of classical point-dipole theory which includes the environmental sensitivity of the electronic polarizability of the ions. According to this picture, the ion in the 12-fold coordination position (e.g., Ba in $BaTiO_3$) plays a relatively minor role electrostatically, its major role being to determine the linear dimensions of the TiO_6 octahedron and consequently to affect the oxygen polarizability and the ease with which the Ti ion may shift from its 6-fold coordination position.

The validity of these ideas may be tested by extending the calculations in this section to other perovskite titanates to see if some underlying unity may be found in the dielectric properties of this class of materials.

SOME PEROVSKITE TITANATES:

$\text{PbTiO}_3, \text{BaTiO}_3, \text{SrTiO}_3, \text{CdTiO}_3, \text{AND } \text{CaTiO}_3$

The striking success of the displaceable-Ti model and the associated calculational methods employed in preceeding sections encourages the extension of these notions to other perovskite titanates. In this section we will consider minimum-energy calculations of the type used in the previous section for the Pb-, Sr-, Cd-, and Ca- titanates, and the necessary force-constant and polarizability-overlap data for these materials will be approximated from the BaTiO_3 data above. We will assume in these estimates that the only differences between these titanates and BaTiO_3 are in the size of the oxygen octahedra in the unpolarized state and in the polarizability of the cation in the Ba site. Furthermore, owing to a lack of accurate optical data on these titanates, we shall assume that the "cubic" oxygen polarizability is the same as in BaTiO_3 (α_0 in Eq(5)).

First, let us see how the necessary force constants, β_1 , β_2 , and γ , may be approximated for these titanates. For an ionic crystal the Born treatment as given by Fowler⁽³⁰⁾ of the potential energy of two ions of charges q_1 and q_2 a distance R apart is assumed to be of the form

$$\phi = q_1 q_2 / R - \mu / R^6 + \lambda / R^9 \quad (35)$$

representing the Coulomb, Van der Waals, and repulsive interactions, respectively. The form of ϕ in Eq (9) is obtained from Eq (35) by summing over a sufficient numbers of nearest neighbors, and by introducing the lattice translation vector, \underline{R}_0 , and the shift of the ion in question from its equilibrium position,

r ; e.g., restricting shifts to be along the z -axis, the Ti-O_a separation is written $R = R_0 \pm Z$ for the O_a ion at $\mp R_0$, respectively. The resulting expression is then expanded in powers of (Z/R_0) to obtain ϕ , Eq (9). Consequently, we may approximate the modified force constant α' for a titanate other than BaTiO_3 , say α' , as $\alpha' \cong \alpha (a/a')^2$, where a and a' are the cell constants for BaTiO_3 and this other titanate, respectively. This approximation amounts to retaining only 1st order terms in the quantity $(a-a')/a'$ ($\leq .06$); correspondingly, $\beta' \cong \beta (a/a')^4$ and $\gamma' \cong \gamma (a/a')^6$.

Now by the same token, the coefficients K_1 , K_2 , and K_3 in Eq (6) may be approximated in the same fashion for some other titanate since as may be seen from Eq (13) the expansion Eq (6) is essentially an expansion in powers of Z .

In order to adjust the BaTiO_3 -data to these other titanates we require cell constant data. These data are known⁽²¹⁾ and are summarized in Table IV. CdTiO_3 and CaTiO_3 (which is the mineral perovskite) are orthorhombic and are usually assigned a multiple unit cell. The data in Table IV show that assuming a cubic unit cell is a good approximation for these materials. Combining these data with Joho's data⁽²³⁾ on cubic BaTiO_3 ($a = 4.002 \text{ \AA}$), we obtain the modified force constants $(\alpha', \beta', \gamma')$ and the α_2 -polarizability coefficients (K'_1, K'_2, K'_3) for each of the four perovskite titanates other than BaTiO_3 . In addition, the unit cell volume which also enters the calculations, Eqs (30), etc., is calculable from the Table IV data, namely $a^3(c/a)$.

Table IV

Perovskite Titanate Data (20°C) (a)

Material	Symmetry	a = b (Å)	c/a	Angle between a and c -Axes
PbTiO ₃	Tetragonal	3.905	1.003	-
SrTiO ₃	Cubic	3.905	-	-
CdTiO ₃	Orthorhombic	3.791	1.004	91°10'
CaTiO ₃	Orthorhombic	3.827	0.999	90°40'

(a) Taken from reference (21).

The α_4 -polarizability data are obtained as follows: the Sr polarizability was determined in a previous paper⁽¹¹⁾, 1.59 Å^3 ; the Ca and Pb values are taken from the article by Tessman et al⁽³¹⁾ as calculated from the refractive indices of CaCl_2 and PbCl_2 , 1.06 and 4.79 Å^3 , respectively; the Cd polarizability is taken for CdF_2 from this same article, 1.75 Å^3 .

We now have sufficient data to use in the same machine program written for the calculations in Section VI. For comparison purposes and in view of the approximate nature of these calculations, only the energy density curves for these titanates were computed, and these curves are shown in Fig. 3. The energy density curve for BaTiO_3 from the previous section is also shown, and in addition the energy density curve corresponding to the (Ti, O_a) Anisotropic Case for BaTiO_3 is also shown in Fig. 3 (dashed curve).

From Fig. 3 we see that at $T = 0^\circ\text{K}$ all titanates shown are ferroelectric in this approximation; whether or not this is the actual case cannot definitely be inferred from Fig. 3 since at low temperatures the quantum-statistical effects must be considered and these are not included in the determination of the partition function in Section IV. The value of Fig. 3 is in the relative nature of the curves. Since the closer in energy the polar and non-polar phases are, the lower the transition temperature expected, we would order the (hypothetical) Curie points of these titanates from Fig. 3 as follows: PbTiO_3 , BaTiO_3 , CdTiO_3 , SrTiO_3 , and CaTiO_3 with decreasing temperature. Let us see what the experimental data indicate: PbTiO_3 has a Curie point at 763°K ⁽³²⁾, and BaTiO_3 at 390°K (Fig. 2); CdTiO_3 has been found to be ferroelectric below 60°K ⁽³³⁾; the dielectric constant of ceramic SrTiO_3 was reported to peak around $20\text{--}30^\circ\text{K}$ by Smolenskii⁽³³⁾, although Hulm⁽³⁴⁾ found no such behavior down to 1.3°K (there is a question of sample purity and preparation in this titanate⁽³⁵⁾); and finally, CaTiO_3 is not ferroelectric⁽²⁷⁾. Consequently, the crude approximations we have employed in this section succeed in correctly establishing the order of the transition temperatures in this group of titanates. For curiosity's sake, the same calculations were performed ignoring the $\alpha_2(P_S)$ dependence and using the adjusted data from the Isotropic case, Table III. These calculations ordered the transition temperatures as: CdTiO_3 , CaTiO_3 , PbTiO_3 , SrTiO_3 , PbTiO_3 , BaTiO_3 with decreasing temperature; practically the reverse order.

VIII DISCUSSION OF RESULTS

The success of the displaceable-Ti model, defined in Section II and employed in following sections with the environmental sensitivity of the O_a polarizability included, in predicting the properties of $BaTiO_3$ and in qualitatively ordering the Curie points of $PbTiO_3$, $BaTiO_3$, $SrTiO_3$, and $CaTiO_3$ indicates that the nature of ferroelectricity in the titanate perovskites as discussed in Section VI represents a reasonable approximation to the truth. The above discussions show that the phenomenon is understandable in terms of point dipole and ionic theory, and that unreasonable values for the polarizabilities and/or effective ionic charges are not needed.

As concerns a model for possible future calculations, the data in Table III and Fig. 3 indicate that the quite simple Ti- O_a model of $BaTiO_3$, which neglects the B_a and O_b polarizations, represents a very good approximation to the actual crystal at room temperature. This model does not contain the objectionable feature of the Ba,Ti, O_a , O_b model of underestimating the total polarization, and in addition, as can be seen from Fig. 3, the energy density curve for this model departs only slightly from the complete model curve at large Ti shifts, and merges with it at small shifts, the critical Ti shift being the same for both curves.

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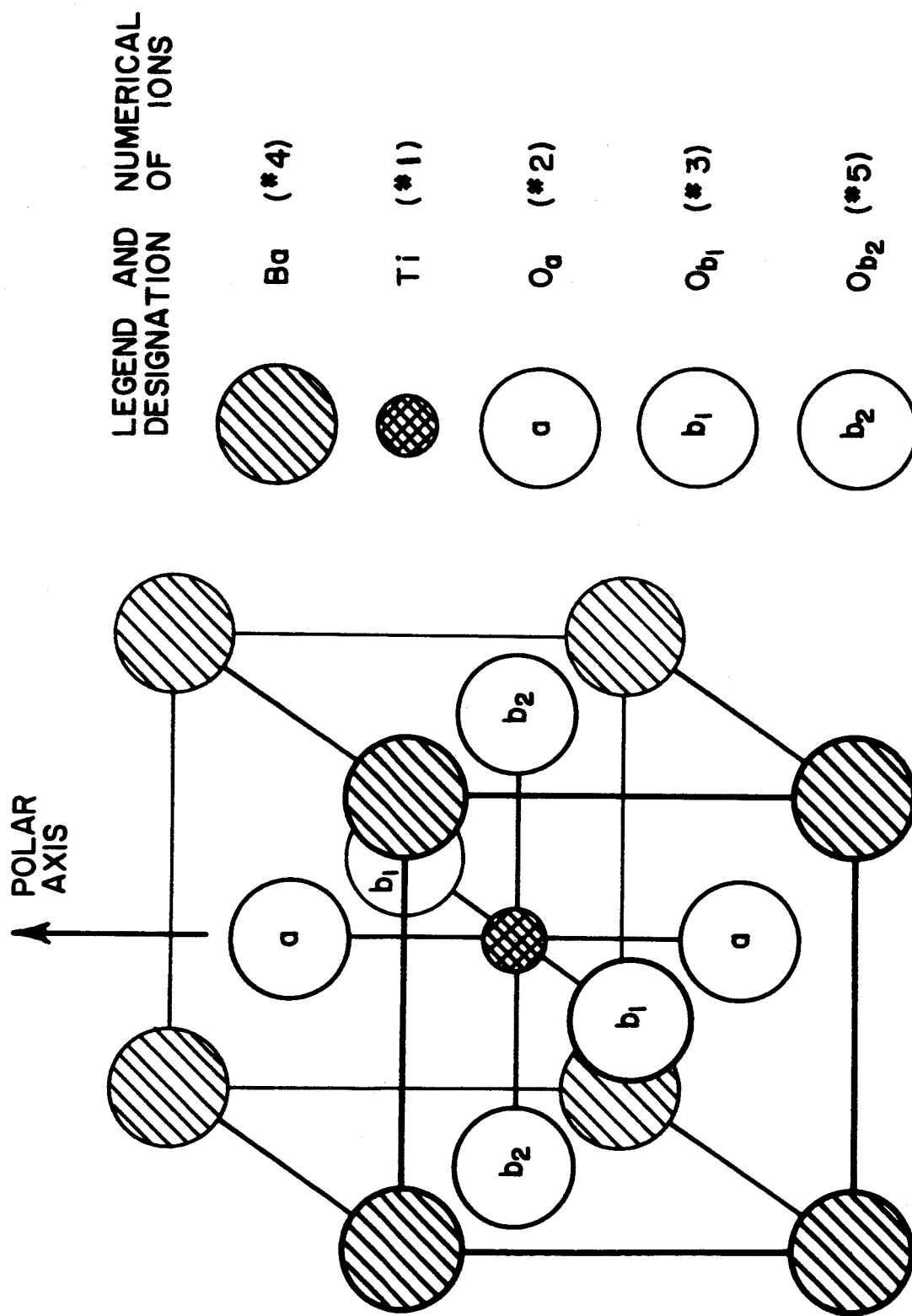


Figure 1

Schematic drawing of perovskite unit cell with numerical ion designation.

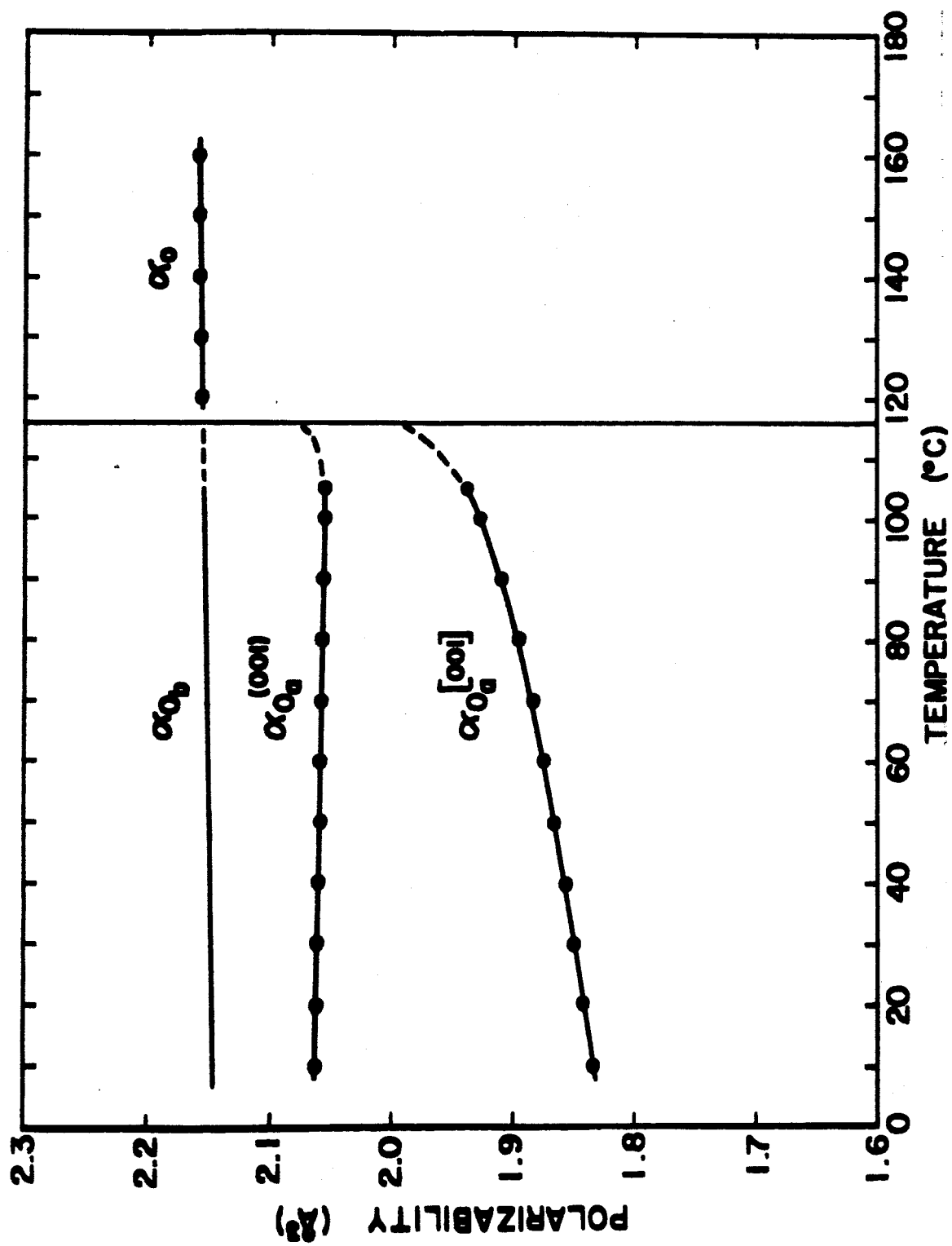


Figure 2

Oxygen polarizability in tetragonal and cubic BaTiO₃ at zero frequency.

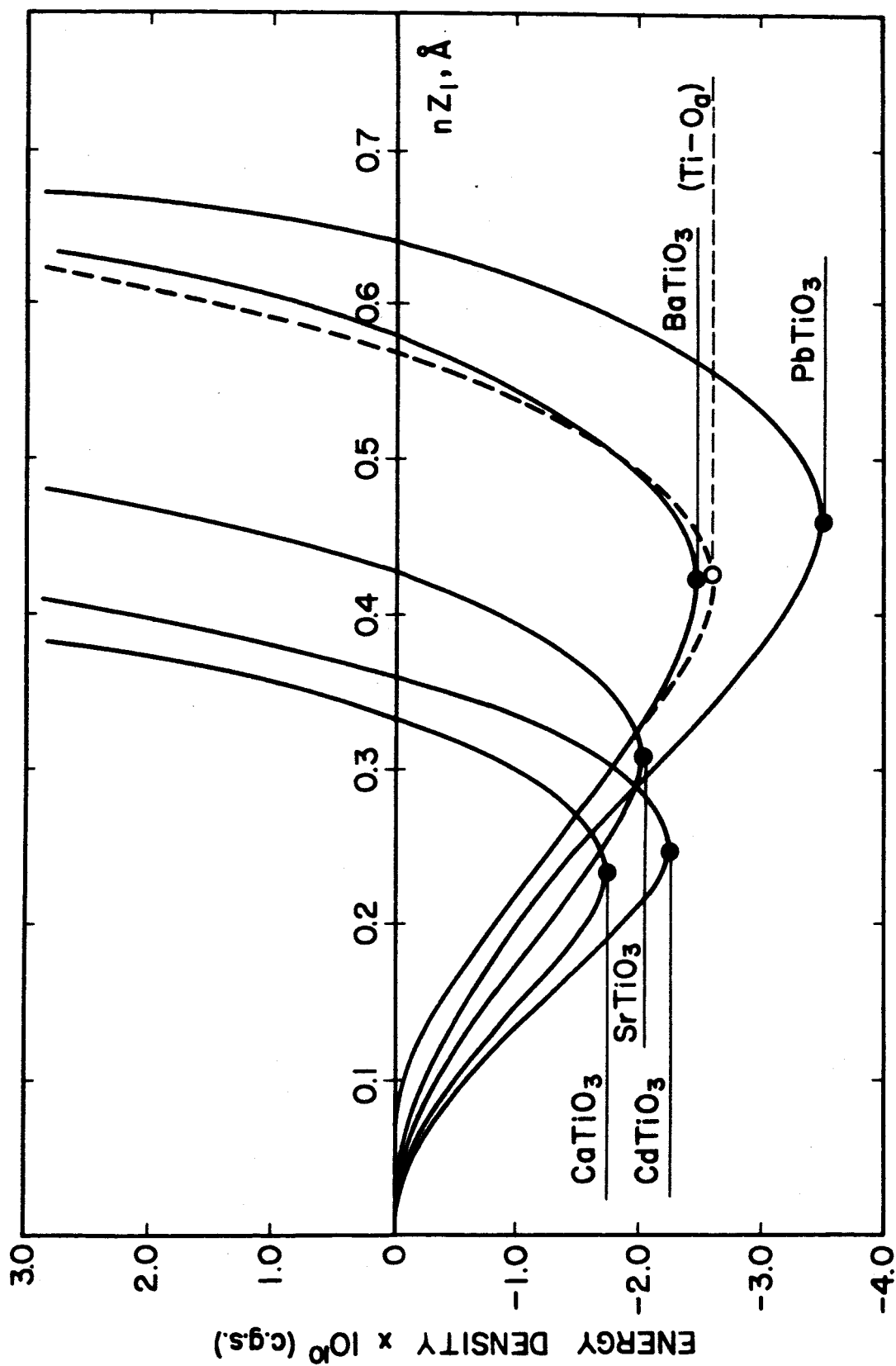


Figure 3

Energy density vs. shift for PbTiO_3 , BaTiO_3 , CdTiO_3 , SrTiO_3 and CaTiO_3 at 0°K .

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Anisotropic Oxygen Polarizability and the Lorentz Correction in BaTiO₃†

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The temperature dependence of the electronic polarizabilities of the ions in BaTiO₃ is incorporated in the Slater-Devonshire theory under the assumption that the dominant contribution arises from the O_h electronic polarizability due to the large Ti-O_h overlap along the polar axis. The temperature dependence of the O_h polarizability as determined from optical data is parameterized in the spontaneous polarization, and a free-energy function for the clamped crystal is derived and compared with the (adjusted) experimental free energy. An internal check on this comparison yields $(dB/dT) = 5.63 \times 10^{-15}$ cgs units, compared with the experimental value 4.5×10^{-15} (B is the fourth-order coefficient in the free energy). A minimum-internal-energy calculation is performed for the clamped crystal polarized along [001], corresponding to the tetragonal phase. This calculation illustrates the role of the O_h polarizability in limiting the spontaneous polarization: Using the O_h polarizability anisotropy data, a spontaneous polarization of 59 600 esu is obtained; if the isotropic oxygen polarizability in the cubic phase is used, 667 000 esu. Similar calculations are performed for the clamped crystal polarized along [011] and [111], corresponding to the orthorhombic and rhombohedral phases, respectively. The O_h polarizability anisotropy data are used, and for the [011] calculation a spontaneous polarization of 33 300 esu is obtained. It is found that the Lorentz correction for the clamped crystal corresponding to a [111] polar axis is not large enough to support a spontaneous polarization, but that a shear of the unit cell of about 27° is required to stabilize a spontaneous polarization along this axis.

INTRODUCTION

THE various molecular theories of ferroelectricity in BaTiO₃ deal, quantitatively or qualitatively, with the Lorentz internal fields in the perovskite lattice and the energy states of the Ti⁴⁺ ion or the TiO₆ octahedra; these theories are reviewed in the book by Jona and Shirane.¹ In particular, the theory due to Slater² considers a displaceable Ti ion in a clamped (zero-strain) BaTiO₃ unit cell and from the classical partition function an expression for the local field at the Ti site is derived. This local field is then used in an analysis of the inner fields including the electronic polarizations, and this analysis permits the external field to be written as a power series in the total polarization; by integration, a free-energy expression for the clamped crystal is obtained. The

salient features of Slater's theory are the enhanced dipole coupling between the Ti and O_h ions along the polar axis (see Fig. 1 which is a schematic drawing of the BaTiO₃ unit cell) and the relatively small role of the Ba and O_c ions in the clamped-crystal approximation.

The phenomenological theory of Devonshire^{3,4} consists of expanding the free energy in a power series of polarizations and strains, or polarizations and stresses, and assuming that this single function applies to the paraelectric and ferroelectric phases. By examining the behavior of certain of the expansion coefficients, the behavior of others can be deduced, and in this fashion Devonshire has accounted for the dielectric, elastic, and piezoelectric properties of BaTiO₃ through three phase changes. These phenomenological free-energy expansions provide the basis for treating experimental data, and, in particular, the free-energy function for the actual crystal (zero stress) can be adjusted to a free-energy function for the clamped crystal for comparison with the molecular-model calculations.

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¹ F. Jona and G. Shirane, *Ferroelectric Crystals* (The Macmillan Company, New York, 1962), Chap. IV.

² J. C. Slater, *Phys. Rev.* **78**, 748 (1950).

³ A. F. Devonshire, *Phil. Mag.* **40**, 1040 (1949).

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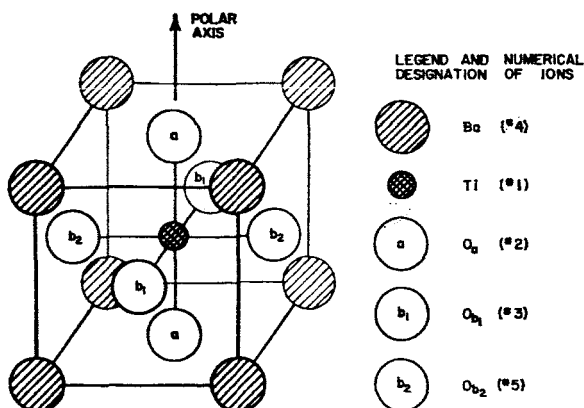


FIG. 1. Schematic drawing of the perovskite unit cell with a numerical ion designation.

The molecular-model calculations for tetragonal BaTiO_3 along the lines of Slater have been based on the assumption that the electronic polarizabilities of the ions are isotropic and temperature independent.⁵⁻⁷ However, there is recent evidence⁸ that the electronic polarizabilities of the ions in BaTiO_3 are altered between the cubic and tetragonal phases because of the interionic overlap that accompanies the ion shifts in the ferroelectric phase. It is found that if the Na-line birefringence at room temperature is calculated by assuming *isotropic* electronic polarizabilities (i.e., from the cubic phase) and by including both the lattice strain and internal sublattice shifts in the geometric Lorentz corrections, a value of 0.0355 found; if the internal sublattice shifts are neglected, 0.0242. The experimental value for the room-temperature birefringence, -0.056 , indicates that the total anisotropy of the electronic polarizabilities contributes the dominant birefringence, -0.082 , and outweighs the strain-and-shift birefringence of 0.035.

The purpose of the present research is to include the temperature dependence of the electronic polarizabilities of the ions in BaTiO_3 in the Slater theory, and thereby to derive a free energy for the clamped crystal for comparison with the adjusted experimental free energy. This comparison will yield both the force constants describing the Ti shift and an internal check on the model and assumptions. Based on these derived force constants, minimum-internal-energy calculations will be performed for the clamped crystal polarized along $[001]$, $[011]$, and $[111]$, corresponding to the tetragonal, orthorhombic, and rhombohedral phases, respectively.

Since experimental data will be employed and since the reported Curie temperatures for BaTiO_3 vary somewhat, the temperature scales for the data used have

been adjusted to a 116°C Curie temperature to coincide with the polarizability data (Fig. 2).

I. OXYGEN POLARIZABILITY ANISOTROPY

The static polarizabilities of the O_a and O_b ions in tetragonal BaTiO_3 are shown in Fig. 2, where $\alpha_{\text{O}_a}^{(001)}$ and $\alpha_{\text{O}_a}^{[001]}$ refer to the O_a polarizability perpendicular and parallel to the polar axis, respectively. These data were derived from the recent⁹ Na-line measurements of the refractive indices in tetragonal and cubic BaTiO_3 and extrapolated to infinite wavelength based on analyses of the dispersions of the indices of SrTiO_3 and TiO_2 (rutile).⁸ In the analysis of these BaTiO_3 optical data, the longitudinal strain of the unit cell ($c/a-1$) was included in the geometric dipole coupling coefficients, and the electronic polarizability anisotropy was attributed entirely to the O_a ion; the reasons for this procedure are as follows: First, as mentioned above, if isotropic polarizabilities are used, then birefringences of 0.0242 and 0.0355 are calculated if the effect of the unit-cell strain, and the effects of the unit-cell strain and the sublattice shifts, are included in the dipole coupling coefficients, respectively. This means that neglecting these sublattice shifts and attributing the polarizability anisotropy entirely to the O_a ion amounts to assuming that the sublattice-shift birefringence of 0.0113 is balanced by the polarizability anisotropies of the ions other than O_a . This is also a necessary assumption because the temperature dependence of the sublattice shifts has not been measured, and, moreover, only one polarizability can be deduced from the optical data. Second, the largest alteration in the electronic polarizabilities is expected for the O_a ion, since the neutron diffraction data¹⁰ indicate a large change

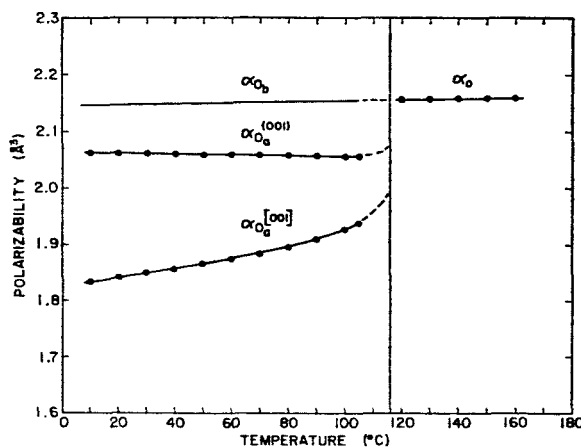


FIG. 2. Anisotropy of the oxygen polarizability in tetragonal BaTiO_3 at infinite wavelength. The superscripts $[001]$ and (001) mean parallel and perpendicular to the polar axis, respectively.

⁵ W. Kinase, Progr. Theoret. Phys. (Kyoto) **13**, 529 (1955).

⁶ S. Triebwasser, J. Phys. Chem. Solids **3**, 53 (1957).

⁷ W. Kinase and H. Takahashi, J. Phys. Soc. Japan **10**, 942 (1955).

⁸ W. N. Lawless, Phys. Rev. (to be published).

⁹ W. N. Lawless and R. C. DeVries, J. Appl. Phys. **35**, 2638 (1964).

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in the Ti-O_a separation between the paraelectric and ferroelectric phases, whereas the O_a and Ba bond lengths are not appreciably altered. Consequently, the α_{O_a} in the tetragonal phase was extrapolated from α_0 in the cubic phase. The data in Fig. 2 are for the temperature ranges 20–105 and 116–160°C; no optical data were taken in the 11°C range below the Curie temperature because of thermal-domain motion.⁹ The recent x-ray data of Joho¹¹ for the c/a ratio and the unit cell volume of the tetragonal phase were used in the analyses shown in Fig. 2.

We now consider the problem of incorporating the temperature dependence of α_{O_a} in the Slater theory of BaTiO₃ (the superscript [001] may be dropped since we are considering the tetragonal phase where the polar axis is the [001] direction). Since the shift of the optical absorption frequency between cubic and tetragonal BaTiO₃ is quite small,^{12,8} and since this absorption is due to an exciton process involving the oxygen polarizability, it follows that the dominant temperature dependence of the O_a polarizability arises from the effect of the Ti-O_a overlap on the infinite wavelength α_{O_a} ; i.e., from the Ti shift relative to the oxygen octahedron. Consequently, if we select the oxygen octahedron as the reference frame for writing the inner field equations (see below), then the temperature dependence of α_{O_a} may be parametrized in terms of the spontaneous polarization P_s as

$$\alpha_{O_a}(P_s) = \alpha_0(1 + K_1 P_s^2 + K_2 P_s^4 + K_3 P_s^6)^{-1}, \quad (1)$$

since the spontaneous polarization depends on the Ti shift. In Eq. (1), α_0 is the isotropic oxygen polarizability in the cubic phase, and only even powers of P_s are involved because the perovskite structure is centrosymmetric. The form of Eq. (1) is chosen to simplify the integration of Eq. (3) below.

The coefficients K_1 , K_2 , and K_3 in Eq. (1) are now determined by combining the $\alpha_{O_a}(T)$ data in Fig. 2 with the $P_s(T)$ data for the tetragonal phase; however, the resulting $\alpha_{O_a}(P_s)$ data are to be used in the *clamped* crystal calculations. We shall approximate these $\alpha_{O_a}(P_s)$ data for the clamped crystal by combining the $\alpha_{O_a}(T)$ and $P_s(T)$ data for the *free* crystal for the following reasons. First, the optical data and hence the $\alpha_{O_a}(T)$ data are for the range 20–105°C for crystals displaying 116°C transition points, and so the $\alpha_{O_a}(P_s)$ data will be for this range also. But the difference between the free and clamped P_s is greatest in the neighborhood of the transition temperature and then decreases rapidly below the transition, the reason being that the free and clamped crystals undergo first- and second-order phase changes. Second, the adjustment of the free P_s to the clamped P_s is very sensitive to the electrostrictive and compliance elements. Consequently, since the $\alpha_{O_a}(P_s)$ expansion does not involve the neighbor-

hood of the Curie point and since an adjustment of the free crystal data is sensitive to experimental data, this approximation is in keeping with the other assumptions and approximations. Combining then with the $P_s(T)$ data due to Merz,¹³ we find, by least-squares fitting,

$$\begin{aligned} K_1 &= 3.31 \times 10^{-11}, & K_2 &= -3.31 \times 10^{-22}, \\ K_3 &= -6.53 \times 10^{-32}. \end{aligned} \quad (2)$$

II. LORENTZ CORRECTION IN BaTiO₃

The nature of the Lorentz correction in BaTiO₃ has been studied by several authors. In Slater's treatment,² the ionic polarization is attributed to the Ti ion, and the local fields are written for the undisplaced ion sites. Cohen¹⁴ criticized Slater's treatment in that the local fields should be written for the actual rather than the undisplaced ion sites. However, Takagi¹⁵ has shown that only the relative sublattice shifts should be considered in the calculation of the inner fields, and Kinase⁵ demonstrated that if relative shifts are considered and if the ionic polarization is attributed to Ti, then a problem mathematically identical to Slater's is obtained when the local fields are written for the actual ion sites. Kinase assumed that each ion carries the same fraction of its full ionic charge. One can go further, however; starting with Takagi's equations and allowing shifts of all the sublattices, it can be shown that an eigenvalue problem of the Slater type for the polarizations results, if the oxygen octahedron is selected as the reference frame and if the oxygen ions are assumed to have the same ionic charge.¹⁶ It is not necessary to assume that all ions have the same fraction of their full ionic charges, and, moreover, the oxygen octahedron is the only sublattice reference frame that can be found in which the inner field equations have this prescribed form. Therefore, the expressions for the local fields given by Slater describe these fields at the actual ion sites and are written relative to the oxygen octahedron and involve the assumptions that the oxygen octahedron shifts as a unit and that the Ba ionic polarization can be neglected. This first assumption is reasonable in light of the neutron diffraction data,¹⁰ and *a posteriori*, the calculations for the tetragonal phase reveal the small role of the Ba polarization. Consequently, adopting the Slater formalism means using an electronic polarizability for the oxygen ions.

We now consider incorporating the anisotropic polarizability data for O_a in the Slater model of BaTiO₃, and, since the details of these calculations are given elsewhere,^{1,2,5,6} we shall review the theoretical considerations and state the results of our calculations. It

¹³ W. J. Merz, Phys. Rev. **91**, 513 (1953).

¹⁴ M. H. Cohen, Phys. Rev. **84**, 368 (1951).

¹⁵ Y. Takagi, in *Proceedings of the International Conference on Theoretical Physics, Kyoto, 1953* (Science Council of Japan, Tokyo, 1954), p. 824.

¹⁶ H. Gränicher (private communication).

¹¹ P. Joho, Z. Krist. **120**, 329 (1964).

¹² R. C. Casella and S. P. Keller, Phys. Rev. **116**, 1469 (1959).

will be convenient to employ a numerical ion designation in what follows, and the schematic drawing of the unit cell, Fig. 1, gives this designation.

Briefly, the Gibbs-type free energy for the clamped crystal has the property that

$$E_0 = (\partial A_p / \partial P_s)_T, \quad (3)$$

where E_0 is the average field in the medium; from the molecular model theory $E_0(P_s)$ is obtained, which allows Eq. (3) to be integrated for the free energy relative to the nonpolar state. The partition function for the Ti ionic polarization is obtained from a potential energy expression for the Ti shift (x, y, z) relative to the oxygen octahedron of the form (cubic symmetry)

$$\phi = a(x^2 + y^2 + z^2) + b_1(x^4 + y^4 + z^4) + c(x^6 + y^6 + z^6) + 2b_2(x^2y^2 + x^2z^2 + y^2z^2) + d_1x^2y^2z^2 + d_2[x^2(y^4 + z^4) + y^2(x^4 + z^4) + z^2(x^4 + y^4)]. \quad (4)$$

From the partition function, the local field at the Ti site is derived in terms of the Ti ionic polarization P_1' relative to the oxygen sublattice; the electronic polarizations of the ions are included by invoking the generalized Lorentz equations for the local field at the i th ion site,

$$E_i = E_0 + \sum_j \left(\frac{4\pi}{3} + T_{ij} \right) P_j + \left(\frac{4\pi}{3} + T_{ii} \right) P_1', \quad i = 1, 2, \dots, 5, \quad (5)$$

where the T_{ij} in Eq. (6) are the geometric Lorentz factors for the perovskite lattice polarized along $[001]^2$ (i.e., $T_{11} = T_{14} = 0$, $T_{12} = 30.080$, $T_{13} = T_{15} = -15.040$, $T_{23} = T_{25} = T_{34} = T_{45} = 4.334$, and $T_{24} = T_{35} = -8.668$, according to the ion designation in Fig. 1), and the $\frac{4\pi}{3}$ is the ordinary Lorentz correction. P_j is the electronic polarization of the j th sublattice, and the numerical ion designation in Fig. 1 implies one ion type per unit cell. Using the polarizability relations (Slater's notation),

$$P_j = X_j E_j / 4\pi, \\ X_j = 4\pi\alpha_j / \tau, \quad (6)$$

where τ is the unit cell volume, the Eqs. (5) are solvable by determinants, and, for the case of the nonlinear O_s polarizability,

$$X_2^{-1} = X_3^{-1}(1 + K_1 P_s^2 + K_2 P_s^4 + K_3 P_s^6) = X_3^{-1}[1 + f(P_s)]. \quad (7)$$

These solutions are given by Slater:

$$E_0 = (C_3/C_5)E_1 + 4\pi(C_4/C_5)P_1'; \quad P_1' = (C_3/C_5)P_s, \quad (8)$$

where C_3 , C_4 , and C_5 are defined in terms of the linear polarizabilities and the geometric Lorentz factors. The inclusion of the P_s dependence of the O_s polarizability,

Eq. (7), alters these coefficients as follows:

$$\begin{aligned} C_3 &\rightarrow C_3 - (C_6 + X_1 C_7) f(P_s), \\ C_4 &\rightarrow C_4 - C_7 f(P_s), \\ C_5 &\rightarrow C_5 - C_8 f(P_s), \end{aligned} \quad (9)$$

where we have used the definitions

$$\begin{aligned} C_6 &= pX_3(X_4 + \frac{1}{2}pX_4 - 1) + \frac{1}{3}X_4 + \frac{2}{3}X_3 - 1, \\ C_7 &= \frac{1}{3} + X_3[\frac{1}{2}q^2(1 - \frac{1}{3}X_4) - \frac{1}{3}(2q - p) - \frac{1}{6}pX_4(2q + p)], \\ C_8 &= X_3(p + q)(1 + \frac{1}{2}pX_4) - (1 + 2pX_3), \end{aligned} \quad (10)$$

the quantities q and p in Eqs. (10) being 2.394 and 0.690.

When the modified coefficients, Eq. (9), are used in Eq. (8), we obtain the $E_0(P_s)$ relation with the effect of the changing O_s polarizability included. This function is then integrated according to Eq. (3) and we find for the free energy relative to the unpolarized crystal:

$$A_p = A(T)P_s^2 + B(T)P_s^4 + C(T)P_s^6, \quad (11)$$

where

$$A(T) = \frac{2\pi C_3 C_4}{C_5^2} + \left(\frac{C_3}{C_5} \right)^2 \frac{\alpha\tau}{e^2} + \left[\frac{C_3^2 \tau (3\beta_1 + 2\beta_2)}{C_5^2 e^2 \alpha} \right] kT, \quad (12)$$

$$\begin{aligned} B(T) &= \left(\frac{C_3}{C_5} \right)^4 \frac{\tau^3 \beta_1}{e^4} + \sigma_1 \left[\left(\frac{C_3}{C_5} \right)^2 \frac{\alpha\tau}{e^2} + \frac{C_3 C_4 \pi}{C_5^2} (C_3 + 1) \right] \\ &\quad + \left[\left(\frac{C_3}{C_5} \right)^4 \frac{15\tau^3}{2e^4 \alpha} \gamma + \left(\frac{C_3}{C_5} \right)^2 \frac{\sigma_1 \tau (3\beta_1 + 2\beta_2)}{e^2 \alpha} \right] kT, \end{aligned} \quad (13)$$

and

$$\begin{aligned} C(T) &= \left(\frac{C_3}{C_5} \right)^6 \frac{\tau^5}{e^6} \gamma + \frac{1}{3} (2\sigma_2 + \sigma_1^2) \left(\frac{C_3}{C_5} \right)^2 \frac{\tau \alpha}{e^2} \\ &\quad + \frac{8}{3} \left(\frac{C_3}{C_5} \right)^4 \frac{\tau^3}{e^4} \beta_1 + \frac{2\pi C_3 C_4}{3C_5^2} (\sigma_2 C_9 + \sigma_2 + C_9 \sigma_1^2) \\ &\quad + \left[\left(\frac{C_3}{C_5} \right)^2 \frac{2\sigma_2 + \sigma_1^2}{3} \left(\frac{3\beta_1 + 2\beta_2}{e^2 \alpha} \right) \right. \\ &\quad \left. + \left(\frac{C_3}{C_5} \right)^4 \frac{20\tau^3 \sigma_1}{e^4 \alpha} \gamma \right] kT. \end{aligned} \quad (14)$$

In arriving at Eqs. (12) through (14), we have set the effective ionic charge of Ti equal to ne and employed the following definitions:

$$\begin{aligned} \alpha &= a/n^2, \quad \beta_1 = b_1/n^4, \quad \beta_2 = b_2/n^4, \quad \gamma = c/n^6, \\ \sigma_1 &= K_1 [C_3 C_8 - C_5 (C_6 + X_1 C_7)] / (C_3 C_5), \\ \sigma_2 &= \frac{\sigma_1 [K_2 + C_8 K_1^2 / C_5]}{K_1}, \quad C_9 = \frac{K_1 (C_4 C_8 - C_5 C_7)}{\sigma_1 C_4 C_5}. \end{aligned} \quad (15)$$

Also, the quantities d_1 and d_2 of Eq. (4) have been assumed approximately equal to c , an assumption which is justified below. Equations (11) represent the free energy function with the changing O_a polarizability included through the σ_1 and σ_2 terms. If $\sigma_1 = \sigma_2 = 0$, the $A(T)$, $B(T)$, and $C(T)$ coefficients reduce to the same as those given by Triebwasser⁶ [Eq. (18)] allowing for the slight notational differences.

This free-energy function is now to be compared with the experimental free energy; however, the experimental constraint (zero stress) differs from the theoretical constraint (zero strain), and this difference must be taken into account. The details of adjusting the experimental function to zero strain have been given by Devonshire^{3,4} and used by Triebwasser,⁶ and these details will not be given here, other than to note that Eq. (24) in Triebwasser's paper is in error by a factor of 2 [see Devonshire's paper, Eq. (10.22)]. Certain experimental data are necessary for this adjustment, and the data used here that differ from the data used by Triebwasser are the following: The coefficient of linear expansion is taken from Joho's accurate x-ray data on cubic $BaTiO_3$ from 120–200°C, 1.083×10^{-5} per degree¹¹; the necessary elements of the electrostrictive tensor were calculated from the spontaneous polarization data of Merz¹³ and the spontaneous strain data of Joho¹¹ for four temperatures around room temperature and the average values found were (cgs units)

$$Q_{11} = 1.17 \times 10^{-12}, \quad Q_{12} = -0.583 \times 10^{-12}.$$

The data for the experimental free energy function are given by Drougard *et al.*,¹⁷ and the static electronic polarizabilities⁸ used for Ba^{2+} and Ti^{4+} were 2.33 and 0.186 \AA^3 . The unit cell volume of $BaTiO_3$ at 120°C was taken from Joho's data, 64.45 \AA^3 .

The adjusted experimental values found for $A(T)$, $B(T)$, and $C(T)$ for use in comparing Eq. (11) are

$$\begin{aligned} A(T) &= 3.72 \times 10^{-5} T - 1.42 \times 10^{-2}, \\ B(T) &= 4.50 \times 10^{-15} T - 1.33 \times 10^{-12}, \\ C(T) &= 9 \times 10^{-23}. \end{aligned} \quad (16)$$

Equations (16) are now combined with Eqs. (11) through (15) to solve for the modified potential energy constants α , β_1 , β_2 , and γ . However, we have more equations than unknowns, and following Triebwasser, we shall use the (dB/dT) equation as an internal check on the model.

These calculations were performed for two cases: an "anisotropic" and an "isotropic" case, where for the latter case σ_1 and σ_2 were set equal to zero in Eqs. (12) through (14) and this, of course, amounts to letting the O_a polarizability be isotropic and equal to the cubic-

TABLE I. Potential energy constants for the Ti shift (cgs units).

	Anisotropic case	Isotropic case ^a
$\alpha = a/n^2$	1.05×10^5	1.05×10^5
$\beta_1 = b_1/n^4$	-8.63×10^{20}	-1.31×10^{19}
$\beta_2 = b_2/n^4$	1.65×10^{21}	3.75×10^{20}
$\gamma = c/n^6$	3.71×10^{36}	3.40×10^{36}
$(dB/dT)^b$	5.63×10^{-15}	0.35×10^{-15}

^a Obtained by neglecting the P_a dependence of the O_a polarizability.

^b Experimental value: 4.5×10^{-15} .

phase oxygen polarizability. The results of these calculations are shown in Table I. To test the sensitivity of the anisotropic case results to the expansion coefficients, Eq. (2), a fourth-order fit to Eq. (1) was performed and the resulting coefficients used in Eqs. (12) through (14). The results were the same as for the sixth-order fit to within a few percent ($\beta_1 = -9.02 \times 10^{20}$, $\beta_2 = 1.71 \times 10^{21}$, $\gamma = 4.46 \times 10^{36}$, and $(dB/dT) = 6.47 \times 10^{-15}$).

Comparing the calculated data in Table I for the two cases, it is seen that the (dB/dT) value for the anisotropic case is in considerably better agreement with the experimental value than (dB/dT) for the isotropic case; this agreement is a valuable internal check on the model and assumptions employed.

From Table I, the effect of the P_a dependence of the O_a polarizability is to "soften" the potential energy; that is, β_1 for the anisotropic case is smaller than for the isotropic case. In neither case, however, does ϕ have a minimum other than the origin. The reason for this alteration in ϕ for small displacements is that the O_a polarizability decreases with the Ti shift. Consequently, for an equivalent Ti shift, the resulting polarization energy for the anisotropic case is larger (smaller negatively) than for the isotropic case, and correspondingly the value of ϕ which balances the negative polarization energy need not be so large for the former as for the latter case.

Triebwasser's treatment of the Lorentz correction in $BaTiO_3$ consisted in performing the above calculations using the neutron-diffraction data for the sublattice shifts; three cases were considered where, in each case, the nonlinear ionic polarizability resulting from ϕ , Eq. (4) was attributed to a different ion (Ti , O_a , or O_b). These calculations assumed the electronic polarizabilities to be linear and isotropic, and the absolute rather than the relative sublattice shifts were considered. Triebwasser found fair agreement for the (dB/dT) calculated for each of these three cases, but these results should be interpreted with caution since only relative sublattice shifts should enter the local fields, and moreover the form of ϕ in Eq. (4) is valid only for a cubic environment, and the O_a and O_b ions do not have this environment. In fact, Triebwasser finds the best agreement between the calculated and experimental values of (dB/dT) for the case of the O_a ion.

¹⁷ M. E. Drougard and E. J. Huibregtse, IBM J. Res. Develop. 1, 318 (1957).

III. ZERO-TEMPERATURE APPROXIMATION FOR TETRAGONAL BaTiO₃

It is of interest to perform a molecular-model calculation for tetragonal BaTiO₃ wherein the internal energy per unit cell is minimized for the clamped crystal; this calculation will employ the polarizability data and potential-energy data derived in the above sections.

The clamped crystal at 0°K should be a good approximation of the actual crystal for two reasons. First, the strain of the unit cell introduces additional ionic polarization and, at the same time, decreases the Lorentz correction at the Ti and O_a sites,⁸ thus decreasing the electronic polarization. Consequently, there is some cancellation between these two effects resulting from the lattice distortion. Secondly, the strain energy terms in the free energy contribute negatively because of the volume expansion at the Curie point, and there is some cancellation between these terms and the positive terms which depend linearly on temperature.

Limiting ourselves to Ti shifts along the *z* axis to correspond with the tetragonal phase, the potential energy per unit volume to be minimized is given by

$$u - u^0 = -\frac{1}{\tau}(az^2 + b_1z^4 + cz^6) - \frac{1}{2}P_1'E_1 - \sum_j \int_0^{P_j} P_j dE_j. \quad (17)$$

The last term in Eq. (17) represents the total electronic polarization energy per unit volume, and u^0 is the unpolarized energy density. The factor $\frac{1}{2}$ in the third term arises from the fact that in the absence of an external field we must count dipole interactions once, not twice. Invoking the polarizability relations, $P_j = (\alpha_j/\tau)E_j$, and writing $z = \tau P_1'/ne$, where τ is the unit cell volume, Eq. (17) becomes

$$u - u^0 = -\frac{\tau}{e^2}[\alpha(P_1')^2 + \beta_1(\tau/e)^2(P_1')^4 + \gamma(\tau/e)^4(P_1')^6] - (\tau/2d_1)P_1P_1' - \frac{1}{2}\sum_{j=2}^5 \frac{\tau}{P_j^2} - \frac{\alpha_3}{2\tau} \int_0^{P_3} \frac{d(E_2^2)}{1+f(P_s)}, \quad (18)$$

where α , β_1 , and γ are the modified force constants discussed in the previous section, and we have used Eq. (7) in the last term of Eq. (18). We may approximate the integral in Eq. (18) by noting that the local field at the O_a site is approximately proportional of the spontaneous polarization, and so this last term in Eq. (18) becomes

$$\simeq -(\alpha_3 E_2^2/2\tau)[1 - \frac{1}{2}K_1P_s^2 - \frac{1}{3}(K_2 - K_1^2)P_s^4 - \frac{1}{4}(K_1^3 + K_3 - 2K_1K_2)P_s^6]. \quad (19)$$

The energy density $u - u^0$ is minimized as follows: For a given value of P_1' , the Eqs. (5) are solved for the P_j and for E_2 using the polarizability relations, and these solutions are substituted in Eq. (18) and (19) to determine $u - u^0$. Perturbing P_1' yields a new value of $u - u^0$, and, in this fashion, the minimum value of $u - u^0$ is determined by a relaxation procedure on a digital com-

puter. In solving Eqs. (5), the $\alpha_{O_a}(P_s)$ relation is of course employed.

These calculations yield the electronic polarizations and P_1' at minimum internal energy, and from $P_1' = (neZ)/\tau$ the equilibrium shift of the Ti ion relative to the oxygen framework may be found, if n is known, the number of effective electronic charges on the Ti ion. Kinase and Takahashi have developed a quantitative molecular theory of the spontaneous deformation of BaTiO₃, and these authors find good agreement with the measured deformation parameters, if n is taken to be 2.12. Alternately, the room-temperature neutron-diffraction data and polarizability data, including the nonlinear O_a polarizability data, can be used to solve for that value of n which yields the room-temperature spontaneous polarization,¹³ 77 000 esu. In this case, however, one solves for the ionicity of the crystal whereby each ion is assumed to carry the same fraction of its full ionic charge. This calculation was performed on a computer which matched the ionicity and the spontaneous polarization, and it was found that an ionicity of 70% yielded 77 000 esu; consequently, for Ti, $n = 2.80$. It is not surprising that this value for n is somewhat larger, since this calculation employs smaller oxygen polarizabilities compared to the previous values used in the literature.

The results of these calculations are shown in Table II with the corresponding experimental data on tetragonal BaTiO₃. It is seen from Table II that the 0°K clamped crystal model of BaTiO₃ that attributes the ionic polarization to the Ti ion and accounts for the nonlinear O_a polarizability represents a quite good approximation to the actual tetragonal crystal; moreover, the results in Table II lend validity to the data derived in previous sections and the assumptions employed.

The same calculations leading to the data in Table II were also performed, ignoring the nonlinearity of the O_a polarizability [i.e., setting $K_1 = K_2 = K_3 = 0$ in Eqs. (1) and (19)] and using the isotropic-case data of Table I. It was found for this case that $P_s = 667$ 000 esu and $Z = 1.5$ Å. These results reveal the sensitivity of the calculations to the oxygen polarizability, since α_3 and α_2 (70 000 esu) from Eq. (1) differ by about 15%, and indicate the incompleteness of any molecular model of BaTiO₃ that neglects the nonlinearity of the oxygen polarizability.

TABLE II. Zero-temperature, clamped-crystal approximation of tetragonal BaTiO₃ (numerical ion designation given in Fig. 1).

Quantity	Calculated	Observed
P_s (esu)	59 600	55 000–78 000
P_1'/P_s	53.2%	...
P_2/P_s	58.4%	...
P_3/P_s	–6.6%	...
P_4/P_s	–5.3%	...
Z , Å	0.15–0.20*	0.14–0.18

* Calculated using an effective ionic charge for Ti of 2.12–2.80.

IV. ZERO-TEMPERATURE APPROXIMATIONS OF ORTHORHOMBIC AND RHOMBOHEDRAL BaTiO₃

The results of the calculations for tetragonal BaTiO₃ in the previous section suggest and encourage similar calculations for the two lower temperature phases of BaTiO₃. On cooling through 5°C, tetragonal BaTiO₃ transforms to an orthorhombic phase with the spontaneous polarization along one of the original cubic $\langle 110 \rangle$ directions, and below -90°C a rhombohedral phase appears with the spontaneous polarization along an original cubic $\langle 111 \rangle$ direction.¹ The potential energy data in Table I can be used to construct ϕ for each of these two phases, and the nonlinear O_a and O_b polarizabilities for these two phases are obtainable from Eqs. (1) and (2) by considering components of the Ti shift along the x , y , and z axes.

A. Orthorhombic Phase

For the orthorhombic phase, we consider a clamped crystal polarized along $[011]$, and it can be shown that for this case

$$(T_{ij})_{\text{ortho}} = -\frac{1}{2}(T_{ij})_{\text{tet}}, \quad (20)$$

where the $(T_{ij})_{\text{tet}}$ correspond to the clamped crystal polarized along $[001]$ and were used above. Because of this simple relation, Eq. (20), the local fields for the tetragonal phase given by Eqs. (5) are correct for this phase also; that is, using the $(T_{ij})_{\text{ortho}}$ in Eqs. (5) describes the local fields at the actual ion sites for the orthorhombic phase.

The clamped-crystal calculations for this phase were programmed for the Ti shift along $[011]$ in the plane of the O_b ions, Fig. 1; α_2 was assumed isotropic and the nonlinearity of α_3 and α_5 was determined from Eqs. (1) and (2). These calculations are a direct extension of the tetragonal phase calculations, and the results are shown in Table III.

It is seen from Table III that the clamped-crystal 0°K approximation based on the molecular model and employing the polarizability and potential energy data yields results in good agreement with the observed data. Moreover, these model calculations indicate that the orthorhombic phase is the lower temperature phase

compared to the tetragonal phase, since the calculated spontaneous polarization for the orthorhombic phase (33 250 esu) is lower than that calculated for the tetragonal phase (59 600 esu).

These results for the orthorhombic phase lend additional support to the model and the data, and the cancellation effects in the free energy discussed above for the tetragonal phase apply here also since there is a volume expansion anomaly in the tetragonal-orthorhombic transition.

Ultimately, the model which attributes the ionic polarization to the Ti ion works as well as it does for the orthorhombic phase because the oxygen octahedron shifts approximately as a unit,¹⁸ as in the tetragonal phase.

B. Rhombohedral Phase

The clamped-crystal model of the rhombohedral phase assumes a cubic cell polarized along $[111]$, and for this case we have

$$(T_{ij})_{\text{rhom}} = 0, \quad (21)$$

so that the Lorentz factors in Eq. (5) reduce to the ordinary Lorentz factor, $4\pi/3$ (~ 4.2). For this case, the O_a , O_{b1} , and O_{b2} ions are equivalent, and Eqs. (5) are solvable by a hand calculation. However, when the internal energy, Eq. (18), is minimized, for this case, with the Ti shift along $[111]$, it is found that the average Lorentz factor must be at least 5.1 for a minimum to exist, using the appropriate potential energy data and nonlinear oxygen polarizability data. That is, these data indicate that the *clamped* crystal at 0°K polarized along $[111]$ is unstable in the dipole approximation.

To interpret this result, it is necessary to bear in mind the reasons why the clamped crystal at 0°K is a good approximation for the tetragonal and orthorhombic phases; namely, the strain polarization is compensated by the reduced electronic polarization for the strained crystal, and the volume expansion anomaly gives rise to negative strain energy terms which compensate the positive temperature terms in the free energy. This is not the case for the rhombohedral phase: There is a volume *contraction* associated with the transition from orthorhombic to rhombohedral,^{19,20} and the strain polarization is relatively much larger because the geometric T_{ij} dipole coupling factors vanish for this case.

Since these calculations show the rhombohedral phase to be unstable in the dipole approximation, it is of interest to carry the calculations to a higher approximation by including the distortion of the unit cell in the T_{ij} factors. This effectively amounts to including

TABLE III. Zero-temperature, clamped-crystal approximation of orthorhombic BaTiO₃ (numerical ion designation given in Fig. 1).

Quantity	Calculated	Observed
P_s (esu)	33 250	42 000 ^a
P_1'/P_s	40.9%	...
P_2/P_s	-11.0%	...
P_3/P_s^b	29.1%	...
P_4/P_s	8.9%	...
$(X^2 + Y^2)^{1/2}$	0.07-0.09 Å	0.13 Å ^c

^a According to Merz (Ref. 21).

^b The O_{b1} and O_{b2} ions are equivalent.

^c According to Shirane (Ref. 18).

¹⁸ G. Shirane, H. Danner, and R. Pepinsky, Phys. Rev. **105**, 856 (1957).

¹⁹ H. F. Kay and P. Vousden, Phil. Mag. **40**, 1019 (1949).

²⁰ G. Shirane and A. Takeda, J. Phys. Soc. Japan **7**, 1 (1952).

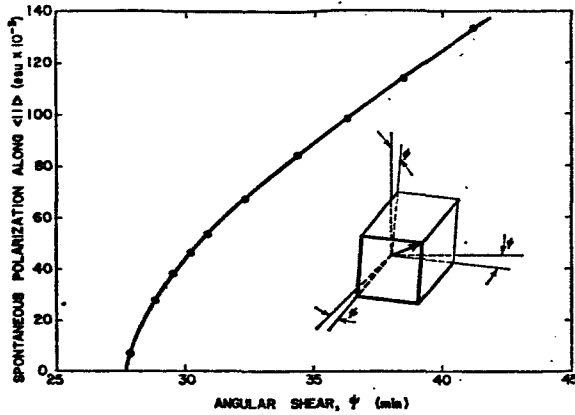


FIG. 3. The role of the angular shear in stabilizing a spontaneous polarization along $[111]$ in rhombohedral BaTiO_3 .

quadrupole terms, since we shall now consider products of electronic moments and ion shifts.

We may approximate the rhombohedral cell as a pseudocubic cell with the original orthogonal axes each sheared by a small angle ψ so as to elongate the cell along $[111]$ which is the polar axis. Consequently, the vector separation between an i th ion at the origin and a j th ion is given by

$$\mathbf{r}_{ij} \cong a_0 [(l+m\psi+n\psi)\mathbf{i} + (m+l\psi+n\psi)\mathbf{j} + (n+l\psi+m\psi)\mathbf{k}], \quad (22)$$

where the translation indices (l, m, n) locate the j th ion relative to the i th ion in the cubic unit cell. The cell constant is a_0 , and the small angle approximation has been used.

Using this vector separation, we find for the geometric Lorentz factors to first order in ψ ,

$$(T_{ij})_{\text{rhomb}} \leq \psi \left[12 \sum_{(l,m,n) \neq (0,0,0)} \frac{n^2}{(l^2+m^2+n^2)^{5/2}} - 4(T_{ij})_{\text{tet}} \right]. \quad (23)$$

In deriving Eq. (23) we have neglected the cross terms which do not come from the near neighbors. The sums indicated in Eq. (23) are easily computed to an accuracy of ± 0.01 , and, by combination with the $(T_{ij})_{\text{tet}}$, the $(T_{ij})_{\text{rhomb}}$ are found. Table IV summarizes these data. We first note from Table IV that the shear of the unit cell appears to increase the Lorentz factors in marked contrast to the tetragonal phase where the longitudinal strain of the unit cell decreases these factors.⁸ In particular, a 1% strain for the tetragonal phase decreases the Ti-O₆ Lorentz factor from 34.27 to 33.68 (ordinary Lorentz correction included), a 1.7% decrease; from Table IV, a 1% shear increases the Ti-O Lorentz factor from 4.19 to 5.59, a 33% increase.

Before turning to the computations for the rhombohedral phase, the question of the ionic polarization must be considered. We shall consider a "pseudo-

clamped" unit cell which has been elongated along the $[111]$ polar axis according to Eq. (22), but only the Ti ion shift from the sheared position will be considered. That is, we will neglect the shift of the other ions from their sheared positions. Consequently, the relative shifts of the ions arising from the shear are asymmetric about any ion position and sum to zero for the near dipole interactions (i.e., the quadrupole ionic polarization terms in ψ^2 sum to zero). The local fields at the ion sites arising from the Ti ionic polarization P_1' are not correctly given by Eq. (5) for the rhombohedral phase, since the form of Eq. (5) results from the symmetry properties of the $(T_{ij})_{\text{tet}}$. Considering the relative shifts between the sheared and shifted Ti sublattice and the other sheared sublattices, we find that the local fields are given by

$$E_{i \neq 1} = \sum_j \left[\frac{4\pi}{3} + (T_{ij})_{\text{rhomb}} \right] P_j + \left[\frac{4\pi}{3} + (T_{i1})_{\text{rhomb}} \right] P_1', \quad (24)$$

$$E_1 = \sum_j \left[\frac{4\pi}{3} + (T_{1j})_{\text{rhomb}} \right] P_j - P_1' \sum_{j=2}^5 \frac{n_j}{n_1} (T_{1j})_{\text{rhomb}},$$

where n_j is the number of effective ionic charges on the j th ion, and the ratios n_j/n_1 are assumed the same as the ratios of the full ionic charges (i.e., each ion is assumed to carry the same fraction of its full ionic charge). In writing down Eqs. (24), we have ignored the ionic polarization resulting from the shear of the unit cell, and instead the ionic polarization is attributed entirely to the P_1' ; the reason for this is that relative to the origin in Eq. (22) the ionic moments of the unit cell associated with the shear cancel exactly.

Using the data of Table IV in Eqs. (24) and employing the appropriate potential energy data and the nonlinear α_2 , α_3 , and α_5 polarizability data, energy minimization computations were programmed for several values of ψ ; the results of these calculations are shown in Fig. 3 which indicates the spontaneous polarization P_s resulting from a given shear ψ .

It is seen from Fig. 3 that the shear of the unit cell has a pronounced effect on the spontaneous polarization along the $[111]$ direction and that this polarization becomes unstable for shear values less than about $27\frac{1}{2}'$.

TABLE IV. Quadrupole coupling coefficients for the rhombohedral unit cell (numerical ion designation given in Fig. 1).

(i, j)	$(T_{ij})_{\text{rhomb}}/\psi$
$i = j$	91.3
$(1, 2), (1, 3), (1, 5)$	140
$(1, 4)$	74.6
$(2, 3), (2, 5), (3, 4), (4, 5)$	94.5
$(2, 4), (3, 5)$	108

in this approximation. A shear of $30'$ yields the observed polarization²¹ of 41 000 esu, and at this shear value the self-consistent local field relations Eq. (24) show that at minimum energy, the contributions of the various polarizations are $P_1'/P_s = 29.1\%$; $P_2/P_s = P_3/P_s = P_5/P_s = 17.1\%$; $P_4/P_s = 17.9\%$. These data indicate a Ti shift of 0.056–0.073 Å along the pseudocubic [111] direction, for $n_1 = 2.12$ –2.80 electronic charges.

The computed shear of $30'$ is in satisfactory agreement with the x-ray value¹⁹ of $8'$, considering the approximations and assumptions used. In particular, the coefficients of the sixth-order terms in Eq. (4) were assumed equal, and this assumption affects the rhombohedral phase calculations more than the tetragonal phase ($x=y=0$) or orthorhombic phase ($z=0$) calculations.

We also note from these data and the data in Tables II and III that the Ba ion plays an increasingly more important role in going from the tetragonal phase ($P_4/P_s = -5.3\%$) through the orthorhombic phase ($P_4/P_s = 8.9\%$) to the rhombohedral phase ($P_4/P_s = 17.9\%$). Consequently, the approximation of neglecting the Ba ionic polarization becomes less valid for these lower temperature phases. This may be seen in Table III where the calculated value of P_s is 20% lower than the observed value, and this is probably due, in part, to neglecting the Ba ionic polarization. Also, the effect of including the Ba ionic polarization in Fig. 3 would be to shift the curve to smaller shears, since from Table IV the Ti-Ba quadrupole interaction is quite large.

V. SUMMARY AND DISCUSSION

In the above sections, we have investigated the polarization dependence of the electronic polarizability of the oxygen ions in ferroelectric BaTiO₃ using data estimated from the optical properties of tetragonal and cubic BaTiO₃. A free-energy function for the clamped crystal was derived and compared to the adjusted experimental function; it was assumed that the $\alpha_{O_s}(P_s)$ data for the free crystal could be used for the clamped crystal in constructing the "clamped-crystal free energy. Minimum energy calculations were performed for the tetragonal, orthorhombic, and rhom-

bohedral phases using the potential energy data derived from the comparison of these free energies.

The agreement between the calculated and experimental (dB/dT) values in Table I (anisotropic case) indicates the importance of the polarizability anisotropy of the O_s ion in the tetragonal phase, and, in particular, the results shown in Table II illustrate the role of this anisotropy in limiting the spontaneous polarization in tetragonal BaTiO₃. The agreement between the calculated and observed data for the spontaneous polarization and Ti shift for the tetragonal, orthorhombic, and rhombohedral phases indicates that these aspects of ferroelectricity in BaTiO₃ can be understood in terms of the point-dipole theory without invoking unreasonable values for the ionic charges or polarizabilities, if the polarizability anisotropy of the oxygen ions is taken into account. The calculations also reveal that the neglect of the Ba ionic polarization is a serious defect of the Slater model for the orthorhombic and rhombohedral phases.

The occurrence of ferroelectricity in solids presents the opportunity of studying dielectric phenomena under conditions which can be more closely controlled and parameterized than in the case of paraelectric crystals. Consequently, the various electro-optic effects can be separated and studied individually, and the electronic polarizability anisotropies deduced in this fashion from optical data may then be used in studies of the low-frequency ferroelectric properties. In this way, the change in the electronic polarizabilities of the ions with polarization, a central problem in dielectric theory, can be investigated directly in ferroelectric crystals.

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²¹ W. J. Merz, Phys. Rev. 76, 1221 (1949).